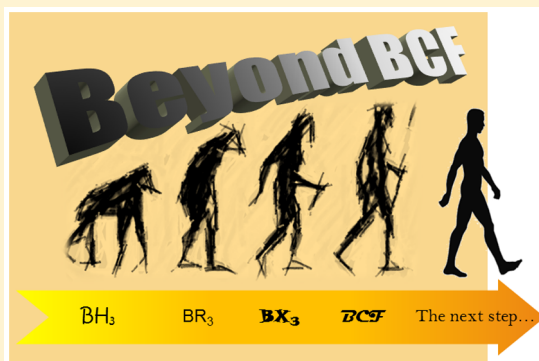


Tris(pentafluorophenyl)borane and Beyond: Modern Advances in Borylation Chemistry

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ABSTRACT: As main-group chemistry, in particular boron chemistry, has expanded and developed over the past 20 years, one reagent has risen to prominence as well. Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ (commonly known as BCF), has demonstrated extensive applications in a wide variety of reactions, including borylation, hydrogenation, hydrosilylation, frustrated Lewis pair (FLP) chemistry, Lewis acid catalysis, and more. The high Lewis acidity of $B(C_6F_5)_3$ is derived from the electronic effects of its three C_6F_5 rings, rendering it a versatile reagent for a great number of reactions. In addition, the steric bulk of these rings also allows it to function as the Lewis acid in a FLP, granting this reagent yet another synthetically useful application. However, as main-group chemistry continues to evolve as a field, new reagents are required that go beyond BCF, increasing not only the range of reactions available but also the breadth of compounds attainable. Great strides have already been made in order to accomplish this task, and this review will highlight modern advances in boron chemistry relating to borylation reactions. Herein, we will show the recent uses of $B(C_6F_5)_3$ in borylation reactions while also focusing on current advances in novel borane and borocation usage that eclipses that of the stalwart $B(C_6F_5)_3$.



INTRODUCTION

Boron reagents are often employed as Lewis acids because of their ubiquitous electrophilic nature. $B(C_6F_5)_3$ ¹ is a powerful Lewis acid because of the electron-withdrawing effects of the three perfluorinated aryl rings and was first synthesized in the 1960s.² Experimental studies probed the Lewis acidity of this borane, the results of which determined that it was comparable to BF_3 although weaker than BCl_3 , falling somewhere between the two, as demonstrated in Figure 1.³

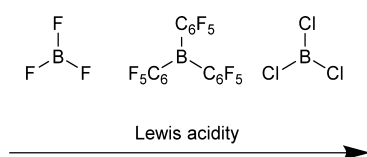


Figure 1. Lewis acidity of boranes.

Furthermore, a multitude of boron Lewis acids, including $B(C_6F_5)_3$, have been studied by examining their hydride- and fluoride-ion affinities.^{4,5} These methods give insight into the relative stability and reactivity of a range of Lewis acids, both experimentally and computationally. Such methodologies are useful because they provide scales upon which a variety of reagents can be placed, allowing the selection of a specific Lewis acid and thus providing a more tailored approach when planning reactions. The inherent electrophilicity of $B(C_6F_5)_3$ makes it suitable for a wide range of reactions, many of which are well documented in the literature.¹ Common uses include

catalysis, with industrial applications in Ziegler–Natta olefin polymerization, where it functions as an activator component.⁶

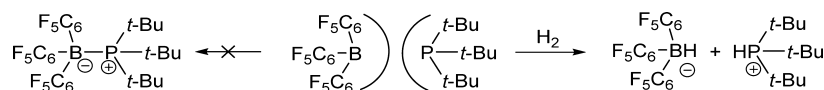
$B(C_6F_5)_3$ and $RB(C_6F_5)_2$ are almost synonymous with frustrated Lewis pair (FLP) chemistry, with a few recent exceptions involving other Lewis acids such as silylium⁷ and phosphonium.⁸ FLPs are composed of sterically encumbered Lewis acids and bases that are unable to form typical adducts and instead undergo reactivity when introduced to various other reagents including inter alia dihydrogen (H_2), alkenes, alkynes, carbon monoxide (CO), and carbon dioxide (CO_2). It is this steric bulk coupled with the electron-withdrawing nature of the three C_6F_5 groups that makes $B(C_6F_5)_3$ the archetypical Lewis acid in FLP chemistry.⁹ Applications of $B(C_6F_5)_3$ containing FLPs include small-molecule activation, such as H_2 , as shown in Scheme 1, along with many others.¹⁰

A variety of other neutral boranes exist in the literature, including trialkyl-, triaryl-, and trihaloboranes, and are well documented in numerous and expansive borylation reactions, which all involve the formation of new B–E bonds, often using a π nucleophile.¹¹ Many early examples of borylation reactions relied on metal catalysis, which incurs the usual problems of potentially high catalyst cost and more difficult purification of the products.¹² Hence, a way to increase the reactivity of boranes to preclude the need for a metal catalyst has been sought. One potential answer to this has been the study of

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Scheme 1. Structure of an FLP



borocations, compounds that were defined over 30 years ago that have evolved into an exciting new field of boron chemistry.¹³ These compounds display high Lewis acidity as a result of the formal positive charge on the boron center.¹⁴ Borocations are frequently defined and characterized by their coordination number, which also denotes a general trend in the relative Lewis acidity, as shown in Figure 2. The 2-coordinate

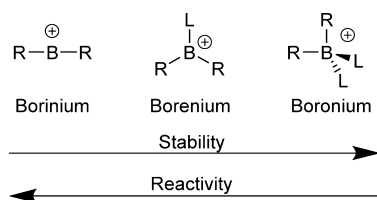


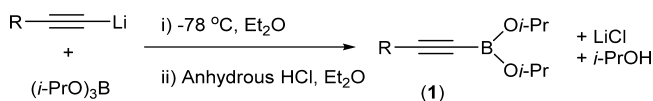
Figure 2. Borocation nomenclature and general trends in their stability and reactivity¹¹

boriniums are the most reactive but are seldom utilized because of their instability. Conversely, 4-coordinate boroniums show high levels of structural stability but suffer poor reactivity because of the fully occupied coordination sphere at boron. Between these two, the 3-coordinate boreniums offer a compromise; they possess the added stability of a donor ligand, which allows much easier manipulation (under an inert atmosphere), while their reactivity is bolstered by the unsaturated coordination sphere. This review provides examples of modern uses of $B(C_6F_5)_3$ in a variety of reactions, in tandem with instances where specific neutral boranes and borocations have expanded this field of chemistry in a variety of borylation reactions.

BORYLATION REACTIONS

One area of borylation chemistry that $B(C_6F_5)_3$ is unsuitable for is that of direct borylation substitution reactions, such as dehydroborylation, wherein a C–H bond is transformed into a C–B bond. Historically, Brown et al. demonstrated that trialkoxyboranes were suitable borylation reagents when combined with lithiated organic species, including alkynes, generating alkynyl boronates (1), as seen in Scheme 2.¹⁵

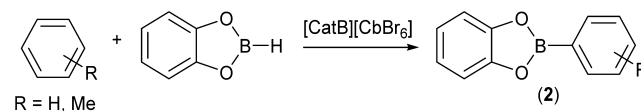
Scheme 2. Borylation of Lithiated Alkynes



A more modern approach avoids the necessity of lithiation by using a base to deprotonate the substrate, which can be either added separately or, in the case of certain borocations, incorporated into the structure of the reagent. Modern advances have shown that certain borenium species are capable of selective dehydroborylation of arenes and heteroarenes. Initial work by Ingleson et al. utilized catechol-ligated borocations for the borylation of benzene derivatives, where a catalytic amount of $[CatB][CbBr_6]$ ($CbBr_6 = [closo-1-H-CB_{11}H_3Br_6]^-$) effectively functions as $[CatB]^+$, catalyzing the

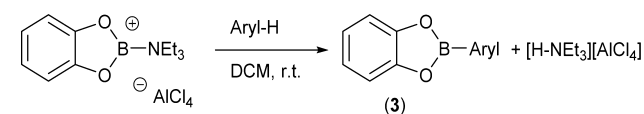
intermolecular arene borylation (Scheme 3) and generating a series of borylated arenes (2).¹⁶

Scheme 3. Dehydroborylation of Arenes



Following this, Ingleson et al. devised a series of amine-ligated catechol boreniums, which were synthesized via halide abstraction of the amine adducts using $AlCl_3$, generating borocations of the general formula $[CatB(L)][AlCl_4]$. When $L = NEt_3$, it was shown that this borenium was capable of dehydroborylation reactions of a variety of arenes, including anilines, indoles, and pyrroles (Scheme 4).¹⁷ Borylation of N-

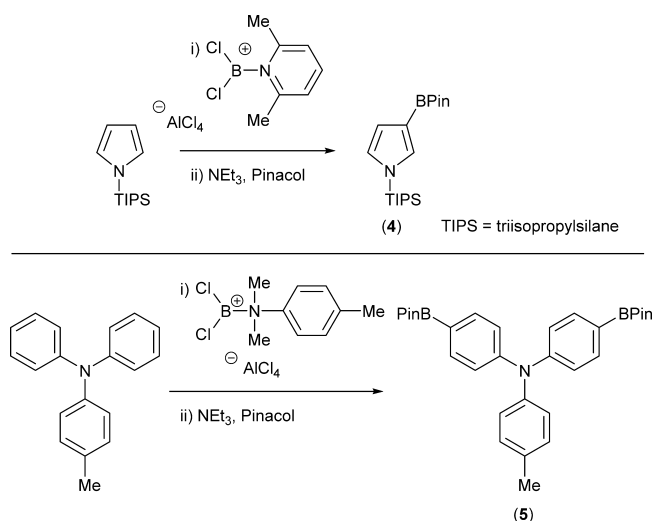
Scheme 4. Dehydroborylation of Arenes with Borocations



heterocycles using boreniums proceeded quantitatively and with excellent regioselectivity. The products (3) could be easily transesterified to yield the pinacolboronate esters as air-stable reagents suitable for further cross-coupling reactions.

In addition to this, more reactive boreniums of the general formula $[Cl_2B(L)][AlCl_4]$ were synthesized and utilized, again in dehydroborylation reactions of arenes, as shown in Scheme 5, such as *N*-TIPS-pyrrole (4).^{18,19} The enhanced electrophilicity of the boreniums was generated by the replacement of the catechol ligand for two halides, which enabled the reactions to proceed swiftly at ambient temperature. In addition, modulation of the Lewis base allowed access to several

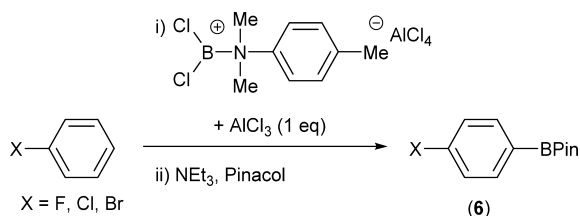
Scheme 5. Dehydroborylation of (Hetero)arenes



diborylated heteroaryl species (5). These were once again isolated as pinacolboronate esters, affording useful synthetic molecules that can be used as critical scaffolds to more complex molecules.

This work was further extended to the borylation of haloarenes,²⁰ which represented a significant step in the expansion of metal-free borylation chemistry because deactivated arenes had been inaccessible using prior approaches.¹⁶ In addition, the borylation of monohaloarenes using this method gave predominantly a single product, the para-substituted isomer (6), demonstrating the control over regioselectivity that this route affords (Scheme 6). It was found that optimal conditions required a second 1 equiv of AlCl₃ and 10 equiv of the haloarene (which was used as the solvent).

Scheme 6. Dehydroborylation of Arenes Using a Borocation



Recently, Fontaine et al. demonstrated a metal-free catalytic approach to arene borylation, using the borane (1-TMP-2-BH₂C₆H₄)₂ (7; TMP = 2,2,6,6-tetramethylpiperidine) as a C–H bond activator.²¹ As depicted in Scheme 7, the borane first reacts with the arene, in this case *N*-methylpyrrole, activating the C–H bond in the 2 position and releasing H₂. This intermediate is subsequently reacted with H-BPin, regenerating the catalyst and producing the desired borylated arene as the pinacolboronate ester (8).

In addition to *N*-substituted pyrroles, the substrate scope was expanded to include indoles, furans, and electron-rich thiophenes, often producing yields in excess of 80%. In most cases, the catalyst loading was 2.5 mol %, and generally the products were obtained as a single isomer. The use of this system highlights the benefits over traditional metal-catalyzed pathways, removing the costly necessity to purge trace metal impurities from the products while retaining the selectivity of the reaction.

Repo et al. has also shown that (2-aminophenyl)boranes (Scheme 8) can induce the dehydroborylation of a number of arenes, heteroarenes, and alkenes, generating borylated species (9).²² This reaction is postulated to proceed via a C–H insertion in an FLP-type fashion, wherein the boron and amine

heterolytically split the C–H bond. This reactivity is promoted by the close proximity of the Lewis acid and base, resulting in a relatively low kinetic barrier to reaction ($\Delta G = 21.0 \text{ kcal mol}^{-1}$ for thiophene). In addition, the borylation reaction was found to be almost thermodynamically neutral, and it was shown that the equilibrium could be easily shifted by increasing the concentration of the substrate or removing the H–R² byproduct from the reaction mixture.

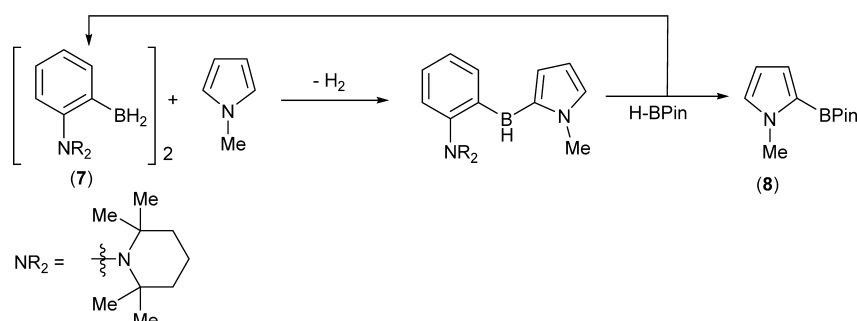
Throughout these examples, the authors have sought to overcome the low reactivity of the substrates without the necessity of “activating” them through methods such as metalation. The relatively low nucleophilicity of the arene substrates was tackled by greatly increasing the electrophilicity of the boron reagents by using borocations, which also provide a source of base to remove the proton, facilitating the dehydroborylation reaction. The FLP pathway allowed access to a catalytic approach, and using H-BPin yields the product as a stable pinacolboronate ester without the need for further reactions.

■ ELEMENTOBORATION REACTIONS

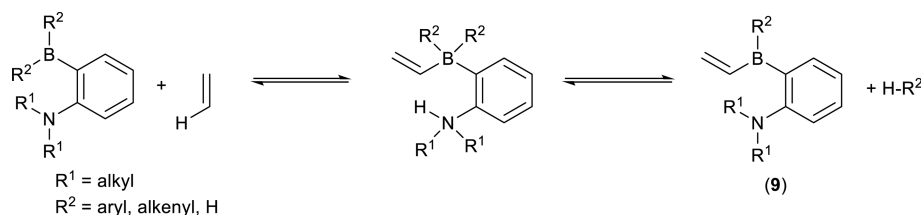
Elementoborations feature the addition of boron and another group to a π system, precluding the need for a substitution reaction to take place. Reports of the 1,*n*-addition ($n = 1–4$) of boron reagents to alkynes are present in the literature,²³ allowing the incorporation of a boron unit while generating a vinyl species, although many historic examples require a metal catalyst.²⁴ These borylated alkenes have been shown to be useful building blocks to more complicated compounds, often utilizing cross-coupling reactions through the boron unit.²⁵ When the scope of these reactions is examined, the shortcomings of B(C₆F₅)₃ are brought into sharp focus; although there are numerous examples of carboboration reactions showcasing B(C₆F₅)₃, the utility of the products is limited by the necessity of –C₆F₅ group transfer and the difficulty to further functionalize through the boron group using cross-coupling reactions, with conditions reported to be more challenging than those of traditional boronic acids and boronate esters.²⁶

To combat this, work by Lappert and Prokai explored alternatives, namely, haloboration reactions, wherein boron and a halogen are added to a π nucleophile, such as an alkyne, generating a vinylboron species.²⁷ Although the resulting products are similar to those of carboboration reactions, the addition of a halogen provides an additional site of functionalization via cross-coupling reactions such as the Suzuki reaction.²⁸ This is advantageous when the desired R group

Scheme 7. Catalytic Dehydroborylation of *N*-Methylpyrrole



Scheme 8. Dehydroborylation of Alkenes



cannot be introduced directly via carboboration and can be instead added to the intermediary compound postborylation.

Until recently, the haloboration reaction was regarded as a niche field within main-group chemistry, with reported examples using haloboranes, such as BCl₃, and terminal alkynes.²⁹ Recent advancements have shown that borocations featuring halides are able to mimic, and even surpass, the reactivity observed with trihaloboranes. The 2-(dimethylamino)pyridine (2-DMAP)-ligated borocation [Cl₂B(2-DMAP)][AlCl₄] (10) was synthesized, with both its structural properties and reactivity being studied.³⁰ This species was identified as a boronium cation found to exhibit reasonable air- and moisture-tolerance, with minimal decomposition after exposure to the atmosphere for 24 h (<5%). Computational studies suggested that the molecule possessed a low energy barrier to ring opening of the highly strained four-membered ring (12.6 kcal mol⁻¹), allowing it to react effectively as a boronium cation in solution, as shown in Figure 3.

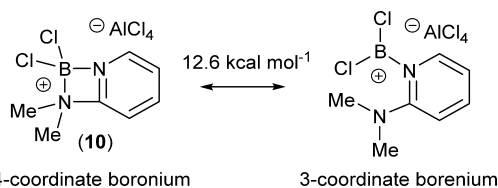
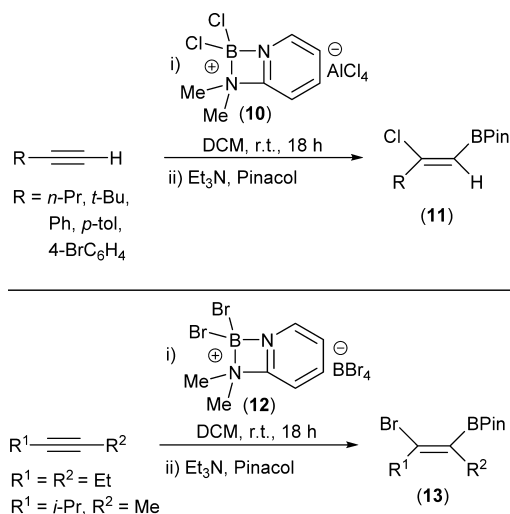


Figure 3. Energy barrier to ring opening of a borocation.

Boronium (10) was shown to undergo selective syn-1,2-haloboration with a range of terminal alkynes, as shown in Scheme 9, and subsequent esterification of the products using pinacol afforded a number of vinylpinacolboranes (11) in good-

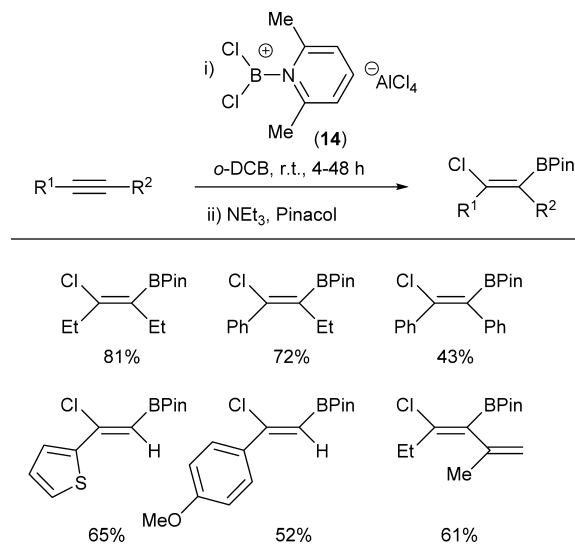
Scheme 9. Haloboration of Alkynes with Borocations



to-high isolated yields (63–88%). In addition, the bromo analogue [Br₂B(2-DMAP)][BBr₄] (12) was shown to undergo haloboration with terminal and certain internal alkynes such as 3-hexyne, generating the bromo-substituted vinylboronate esters (13).

By greatly increasing the Lewis acidity of the borocation, 1,2-haloboration of a range of internal alkynes could be achieved. By using the borenium [Cl₂B(lut)][AlCl₄] (14; lut = 2,6-lutidine), several new vinylboron species were isolated as pinacolboronate esters. The system was shown to be compatible with a range of internal alkynes, featuring a mixture of aliphatic and/or aromatic moieties as well as demonstrating functional-group tolerance of thiophenes and anisoles (Scheme 10). When enynes were employed as targets, haloboration

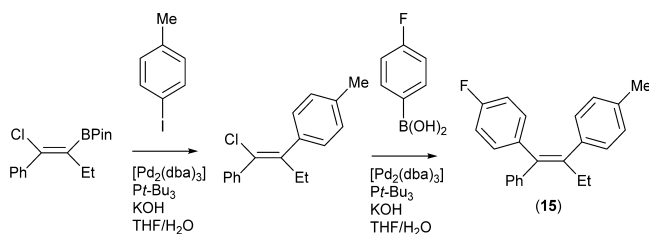
Scheme 10. Haloboration of Internal Alkynes



occurred exclusively at the alkyne site, leaving the alkene functionality untouched. Again, these products were isolated as single regio- and stereoisomers, showing the specificity of this reaction and demonstrating that it is a useful pathway to creating highly functionalized substituted alkenes.

The utility of these products was established by sequential cross-coupling reactions of the vinylboron and chloro substituents, with subsequent Suzuki cross-coupling reactions employed to generate the highly functionalized alkene (15) shown in Scheme 11.¹⁴ It was shown that the reaction was possible in a one-pot fashion, from alkyne to fully substituted alkene. These tetrasubstituted alkenes are known to be structural analogues and precursors to several drug molecules, such as Tamoxifen, a powerful anticancer agent, and Zuclomiphene, a selective estrogen receptor modulator, further demonstrating the value of this reaction pathway.³¹

Scheme 11. Sequential Cross-Coupling of Haloboration Products



Carboration reactions allow for the facile formation of both new C–B and C–C bonds across a π system.³² A variety of trialkylboranes have historically been shown to undergo carboration with certain activated alkynes, such as the work of Wrackmeyer et al.;³³ however, more recently $B(C_6F_5)_3$ has demonstrated a proclivity for these reactions without the need of activated alkynes.³⁴ One of the simplest examples is that of $B(C_6F_5)_3$ and phenylacetylene; 1,1-carboration occurs nearly instantaneously at ambient temperature, although this generates a mixture of *E* and *Z* isomers, as seen in Scheme 12. Photoisomerization can be used to generate the single isomer (16).

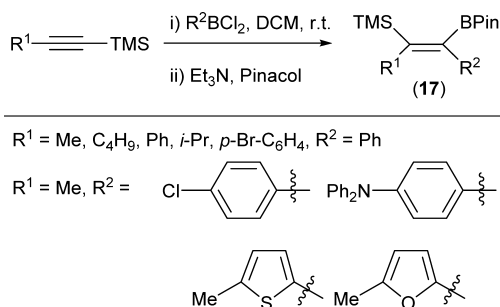
However, $B(C_6F_5)_3$ is unsuitable for carbaborations where the desired product does not feature a C_6F_5 group. Modification of $B(C_6F_5)_3$ to combat this problem has been reported, with $R-B(C_6F_5)_2$ reagents synthesized and employed in carboration reactions, with some reports of selective R-group transfer (as opposed to C_6F_5 transfer).³⁵ Unfortunately, this still leaves a $-B(C_6F_5)_2$ group present in the molecule, hindering further functionalization because of the challenging nature of the cross-coupling reaction with this boron species and requiring higher temperatures and generating lower yields than with boronate esters.²⁴

As such, modern advances have shown that a range of heteroleptic boranes and borocations can be synthesized and applied in various carboration reactions, to be discussed herein. Advantages reported include variation of the R-group transferred to the alkyne, control over the *stereo*- and *regio*selectivity of the reaction, and widened substrate scope. Although 1,1-carboration of activated alkynes (those which feature a suitable migratory group such as silicon, lead, tin, etc.) was developed by Wrackmeyer et al.,^{36,37} these reports generally featured trialkylboranes as the borylation reagent. Modern advances have sought to broaden the scope of application, a selection of which shall now be discussed.

It was shown by Ingleson et al. that neutral borane species of the general formula Cl_2B -aryl could be utilized for the 1,1-carboration of trimethylsilyl (TMS)-substituted alkynes.³⁸ Although similar to earlier carbaborations of activated alkynes, this method introduces a $-BCl_2$ group, which is capable of

being converted to a boronate ester, which is more synthetically useful than the products of trialkyl/arylboranes. Commercially available $PhBCl_2$ was combined with a variety of TMS-alkynes, producing single-vinylborane products with excellent *stereo*- and *regio*selectivity, which were isolable as pinacolboronates (17; Scheme 13). A range of these air-stable products were isolated,

Scheme 13. Carboration of TMS-alkynes

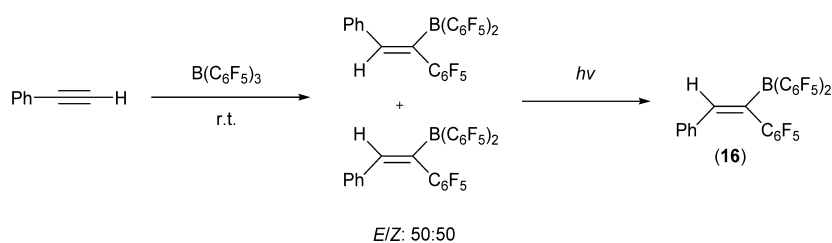


with some structures being confirmed by X-ray crystallography. In addition to $PhBCl_2$, other dichloroboranes were synthesized featuring arenes (*p*-chlorobenzene and triphenylamine) in addition to heteroarenes such as thiophene and furan. These were also shown to be compatible with the 1,1-carboration reactivity observed with TMS-alkynes, allowing access to a variety of vinylboranes featuring several (hetero)aryl groups.

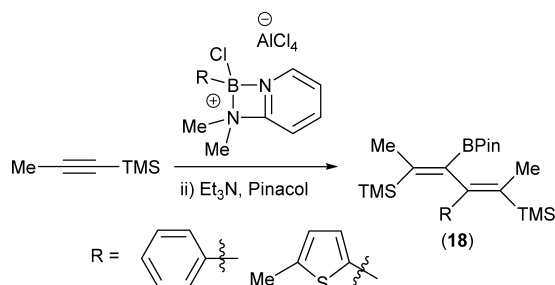
Within the same body of work, the analogous reactivity was observed with borocations of the general formula $[RBCl(2-DMAP)][AlCl_4]$, which are derived from $RBCl_2$ -boranes. However, while additional competitive reactivity with TMS-alkynes prevented the more electrophilic borocation from surpassing the effectiveness of the neutral borane, it did allow access to an alternate reaction pathway and a new species of product. Modification of the reaction conditions to use an excess of TMS-alkynes generated a mixture of products that, postesterification, could be separated via column chromatography. In addition to the 1,1-carboration product, a species shown to be 2-bora-1,3-diene had also been generated (18; Scheme 14). This species has been shown to be accessible with either a phenyl group or a 2-methylthiophene in the 3 position of the diene.

The 1,2-carboration of alkynes, in contrast to haloboration, is scarcely reported in the literature, with some instances of metal-catalyzed carboration reported.³⁹ However, some recent examples are known that use boranes and borocations. Ingleson et al. generated quinolatoboreniums (19), which, when exposed to 3-hexyne, underwent 1,2-carboration, transferring either a phenyl or a thiophenyl moiety, with the subsequent products esterified with pinacol to give the isolated vinylboronates (20; Scheme 15).⁴⁰

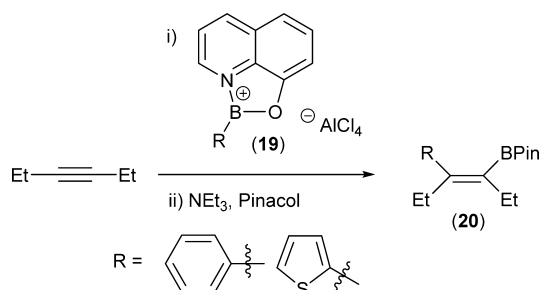
Scheme 12. Carboration of Phenylacetylene with $B(C_6F_5)_3$



Scheme 14. Synthesis of 2-Boradienes

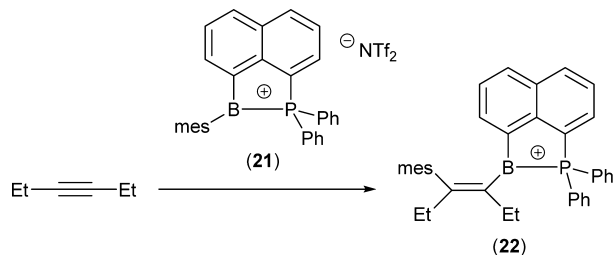


Scheme 15. 1,2-Carboration of 3-Hexyne with a Borocation



Another example of 1,2-carboration using boreniums was reported by Bourissou et al., wherein a phosphorus-coordinated borenium (21) reacted readily with 3-hexyne (Scheme 16).⁴¹ In

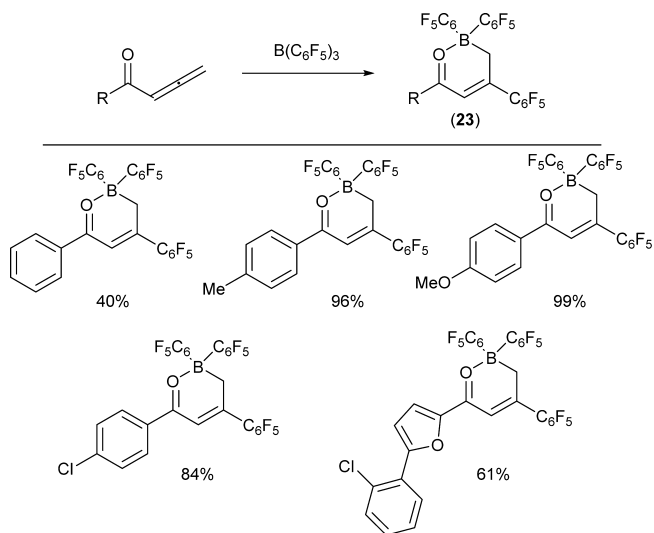
Scheme 16. 1,2-Carboration of 3-Hexyne



this case, a mesityl (mes) group was transferred, selectively generating the vinylboron species (22), as shown in Scheme 16. The reagent represented a novel borenium species, which uses the naphthalene scaffold to create a strong intramolecular B–P interaction. It was reported to be stable but highly reactive, undergoing not only the carboration of 3-hexyne but also the activation of H₂ and demonstrating the broad utility that borocations can possess.

The 1,2-carboration of allenes using boranes was recently reported by Melen et al.⁴² It was shown that the reactions of allenyl ketones and esters solely in the presence of B(C₆F₅)₃ afforded formation of the 1,2-carboration products (Scheme 17). Of note, the stoichiometric reactions with allenyl ketones proceeded extremely rapidly (<30 min) at room temperature with structural analysis via X-ray crystallography, confirming the intramolecularly chelating cyclic dihydroxyborinane products (23).

The breadth of highly functionalized borylated species has expanded greatly in direct correlation with the expansion of elementoboration reactions. Haloboration has moved from an esoteric reaction only observed with haloboranes to a useful synthetic tool, thanks to the rise of borocation chemistry.

Scheme 17. 1,2-Carboration of Allenyl Ketones Using B(C₆F₅)₃

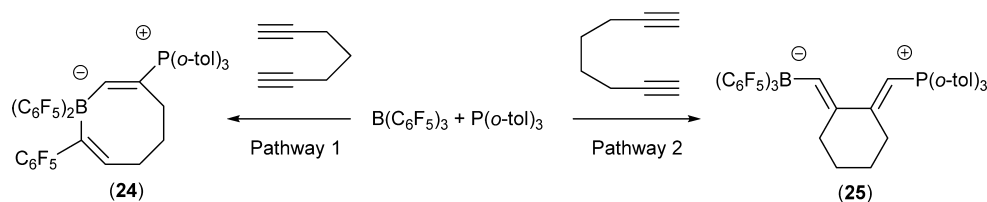
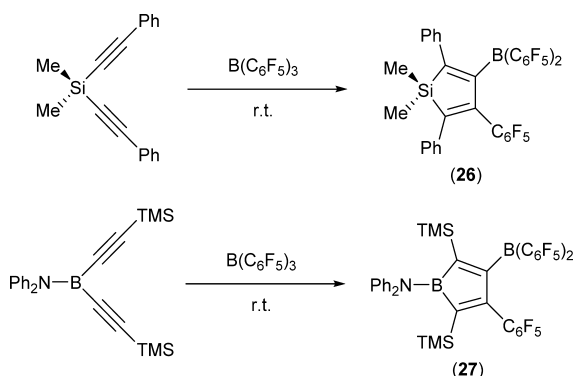
Because an increase in the Lewis acidity of the borocation was vital to expanding the substrate scope, it is probable that future developments will seek to follow this path in the development of new reagents. The main benefit of carboration (delivery of a specific R group to a specific site) is also the area with the largest potential for expansion. By the synthesis of boron reagents that can deliver a plethora of groups, the subsequent variety of functionalizable products greatly increases.

■ BORYLATIVE CYCLIZATIONS

Borylative cyclization reactions have shown great promise in the synthesis of new boron-containing heterocycles and are becoming more prevalent in the literature, with recent examples discussed herein. While the aforementioned reactions of allenyl ketones and esters with B(C₆F₅)₃ afford selective formation of the 1,2-carboration products with cyclization induced by new B–C bond formation and B–O chelation, there exist several reports of reactions that add boron and also generate new C–C bonds. Such work by Erker et al. has shown to induce a variety of cyclization mechanisms, most notably with diyne-derived precursors. One such example used B(C₆F₅)₃ as the Lewis acid component of an FLP in combination with a bulky phosphine [P(*o*-tol)₃], which induced cyclization with different reactivity being observed depending on the substrate.⁴³ For both 1,6-heptadiyne and 1,7-octadiyne, cyclization and the addition of both boron and phosphorus took place, but the resultant ring size and constituent atoms differed, as shown in Scheme 18. In the case of 1,6-heptadiyne, the reaction proceeded as 1,1-carboration of the first alkyne group, followed by 1,2-FLP addition to the other, generating a zwitterionic phosphonium borate containing an eight-membered heterocycle (24; pathway 1). With 1,7-octadiyne, both boron and phosphorus groups are added at the terminal end of the alkynes, inducing cyclization to produce a six-membered cyclic compound (25; pathway 2).

It was also demonstrated that diynes featuring heteroatoms, such as silicon, generate heterocycles (i.e., siloles) via the use of B(C₆F₅)₃, which was used to overcome challenging reaction conditions previously reported with other boranes.⁴⁴ In these reactions, 1,1-carboration of the first alkyne is followed by 1,1-vinylboration of the second. This generates the silole product (26), shown in Scheme 19.⁴⁵ Similar reactivity has also

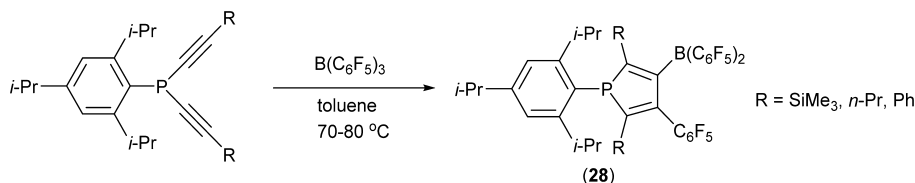
Scheme 18. Cyclization of Diynes Using FLPs

Scheme 19. Generation of Heterocycles from Diynes Using B(C₆F₅)₃

been observed with other group 14 elements, with reports of the synthesis of germanium-, tin-, and lead-containing heterocycles synthesized with trialkylboranes.⁴⁶ Although the reaction proceeded well under mild conditions, the use of B(C₆F₅)₃ forces the incorporation of a C₆F₅ group into the structure of the heterocycle, potentially reducing the general synthetic attractiveness of such a methodology. Similar reactivity was also observed, where boroles (27) were synthesized from a boron-containing diyne bis[(trimethylsilyl)ethynyl]diphenylaminoborane and B(C₆F₅)₃.⁴⁷

In addition, a comparable reaction can be used to access phospholes, for which few synthetic routes are reported.⁴⁸ These five-membered heterocycles have applications in materials science,⁴⁹ particularly when boron-based acceptor substituents are in conjugation with the phosphorus donor.⁵⁰ Hence, the 3-boryl-substituted phospholes (28) shown in Scheme 20 are of significant interest. They are synthesized from the respective bis(alkynyl)phosphine in combination with B(C₆F₅)₃, resulting in a 1,1-carboration reaction sequence.⁵¹

Tsao and Stephan have demonstrated the application of boranes in the synthesis of tellurium-containing heterocycles,⁵² which prove to be desirable as both catalysts⁵³ and for their optoelectronic properties.⁵⁴ When a tellurium acetylide was used, 1,1-carboration reactions with B(C₆F₅)₃ and other boranes were reported, generating boron-containing vinylic telluroethers (29). Subsequent exposure to phenylacetylene generated the zwitterionic-heterocyclic products (30), seen in

Scheme 20. Generation of Phospholes Using B(C₆F₅)₃

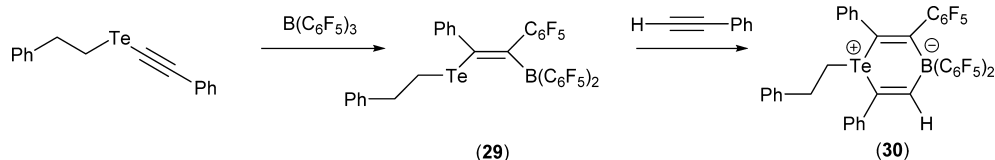
Scheme 21, with the vinyl species acting as an intramolecular FLP.

Following this work, it was reported that exposing a diethynyltellurium compound to various boranes also generates similar heterocyclic products.⁵⁵ The reaction between the tellurium diyne and borane once again begins with 1,1-carboration, forming 31, which can then undergo either a second intramolecular 1,1-carboration, forming 32, or alternatively an intermolecular FLP addition generates 33 (Scheme 22). The products of the former reaction (32) are currently being investigated as novel tellurium heterocycles containing an electrophilic unit within the ring, giving rise to attractive future applications in optoelectronic materials.

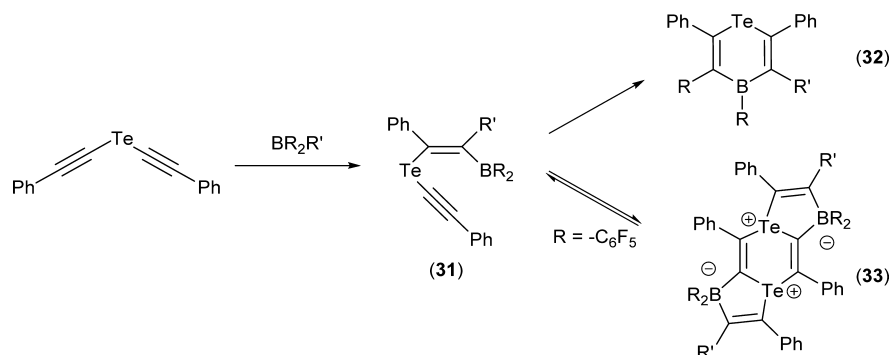
This reactivity can be directly compared to similar work involving bis(dialkynyl) sulfides and borane reagents.⁵⁶ Variation of the alkynyl substituent was found to alter the reaction outcome with boranes. With bis(phenylethynyl) sulfide (34) and B(C₆F₅)₃, a 2:1 molar ratio reaction occurs to generate a benzothiophene derivative (35). However, when bis(*tert*-butylethynyl) sulfide (36) is used, boranes of the formula R–B(C₆F₅)₂ trigger cyclization to form the five-membered thiophenes (37; Scheme 23). Such a reaction is posited to proceed via two successive carbaborations: first of an alkynyl unit and then vinylboration of the second. This reactivity is in stark contrast to that observed with the tellurium diynes because under these conditions no boron insertion into the ring occurs.

While diynes have been shown to allow multiple pathways to new cyclic species, many examples of borylative cyclization exist that use other substrates. Enynes, constituting both alkyne and alkene fragments, have been targeted for cyclization reactions as well. The reaction between B(C₆F₅)₃ and a series of 1,6-enynes was shown to generate novel borylated cyclic species (Scheme 24).⁵⁷ The reaction proceeds by first generating a multicyclic species (38) via cyclopropanation with simultaneous 1,1-carboration, the major diastereomer of which can be isolated via crystallization. These species can subsequently undergo a ring-opening reaction of the newly generated cyclopropane, which can either yield cyclopentane (39) or cyclohexane (40) derivatives, depending on which C–C bond is broken (Scheme 24). It was determined that substitution of the alkene of the initial enyne determined which cyclic product is formed, with both products being the result of a net 1,4-carboration reaction.

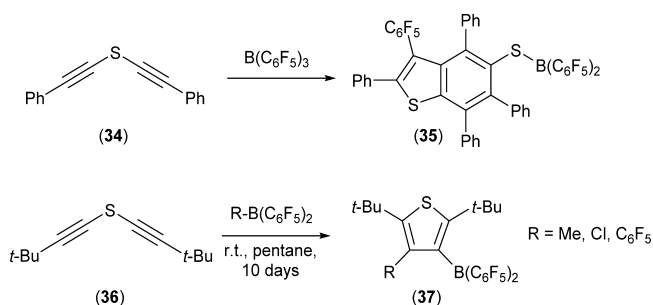
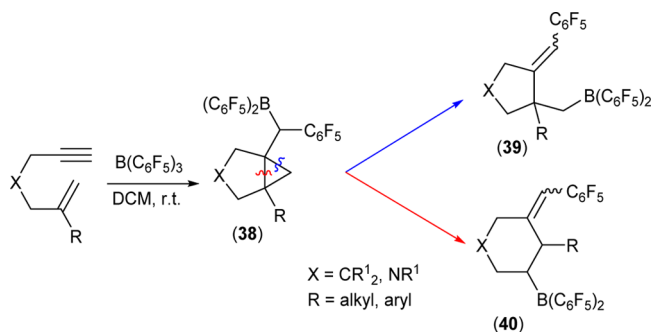
Scheme 21. Borylative Cyclization of Alkynyltellurides



Scheme 22. Cyclizations of Tellurium Diynes



Scheme 23. Generation of Thiophenes from Cyclizations of Sulfur Diynes

Scheme 24. Cyclopropanation/Carboration Reactions of Enynes with B(C₆F₅)₃

Erker et al. have also used B(C₆F₅)₃ to synthesize boracycles from dicyclopnylacetylene in an interesting ring-opening mechanism similar to that discussed previously.⁵⁸ Upon addition, the compounds undergo successive 1,1-carboration reactions, with transfer of two of the C₆F₅ groups, to form dihydroboroles, as shown in Scheme 25. The way in which the cyclopropyl ring opens determines the structural conformation of the resulting intermediate, leading to two distinct products. In pathway 1, the ring opens to generate an “isopropene” group, leading to two chiral centers in 41, whereas in pathway 2, an “n-propene” group is formed, leading to a single chiral center in 42.

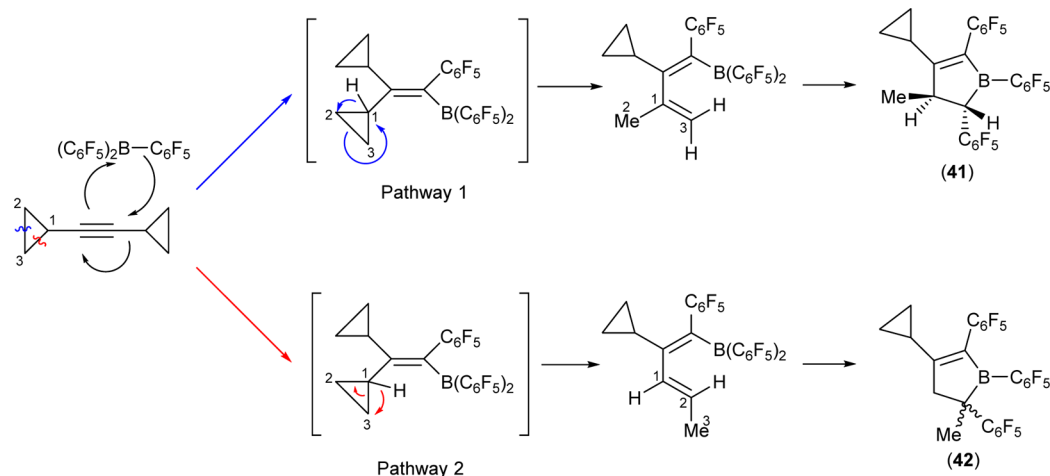
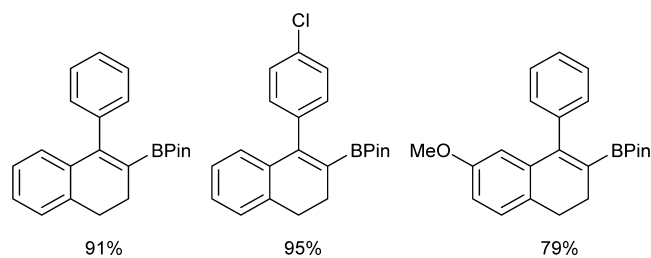
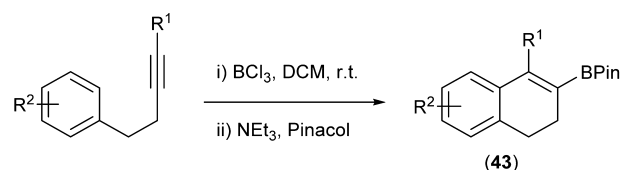
Recently, it has been shown that the strong Lewis acid BCl₃ can be applied in borylative cyclizations of a range of 4-arylbutynes, producing 1-aryl-2-boro-3,4-dihydronaphthalenes (43), as shown in Scheme 26. These contain structural groups prevalent in biologically active agents and pharmaceuticals.⁵⁹ Although only select examples are shown here, >20 products are reported in good-to-excellent yield, showing the versatility of this reaction. By using an inexpensive reagent [relative to B(C₆F₅)₃] in the form of BCl₃ and avoiding the use of transition metals, the author has shown a readily accessible pathway to synthetically useful C(sp²)-boronate esters.

The utility of these products was demonstrated 2-fold in Scheme 27; in the first instance, it was shown that cross-coupling with 4-bromotoluene proceeded readily to give 44 in good yield, and second that the borylated products can be dehydrogenated to give the borylated naphthalene analogue (45). The ability to create highly functionalized molecules from commercially available starting materials is of great importance in synthetic chemistry, with the products synthesized here posing as potential intermediates in the synthesis of pharmaceuticals such as Nafoxidine.⁶⁰

Propargyl esters, amides, ureas, carbonates, and carbamates (Figure 4) are structurally well equipped to undergo a variety of reactions, but of particular importance is their propensity to undergo cyclization reactions. The hard Lewis basic oxygen is capable of coordinating to a boron Lewis acid, holding it in close proximity to the alkyne moiety, increasing the propensity for further reactivity. We will now examine multiple examples of cyclization reactions of these propargyl-functionalized substrates.

The reaction between propargylamides and B(C₆F₅)₃ was shown to generate a number of differing cyclic products; however, slight variances in the structure of the amide reagent affected the reactivity observed.⁶¹ While a range of propargylamides were found to undergo cyclization reactions with B(C₆F₅)₃, forming 46, disubstitution in the propargylic position results in a 1,1-carboration product instead (47), because of the high level of 1,3-allylic strain that would arise from the cyclized species (which is only observed as a minor product). In the case where R³ = H (Scheme 28),

Scheme 25. Cyclization of Dicyclopopylacetylene

Scheme 26. Cyclization of 4-Arylbutynes Using BCl_3 with Select Examples of Functional-Group Variance

protodeboronation of species **46** can occur to give the oxazole derivative following isomerization (**48**). These oxazole products represent a useful synthetic building block because numerous natural products, drugs, and pharmaceuticals contain this heterocycle.⁶² Traditionally accessed using transition-metal catalysis,⁶³ this metal-free synthesis represents an attractive alternative.

The proclivity of the isolobal propargyl esters to undergo borylative cyclizations has been probed extensively, and it has been shown that they are useful materials for the synthesis of 1,3-dioxolium salts and allylboron reagents.⁶⁴ In the case of internal propargyl esters ($\text{R}^2 = \text{Me}$, *n*-Pr; Scheme 29), $\text{B}(\text{C}_6\text{F}_5)_3$ was used to induce cyclization and produce the zwitterionic 1,3-dioxolium salt (**49**). Several examples were synthesized, and a mechanism was postulated that involved an initial borylative

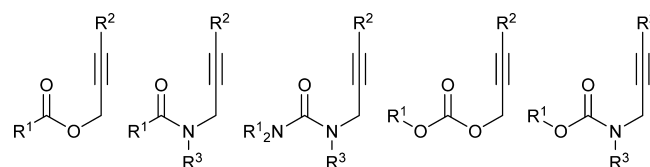


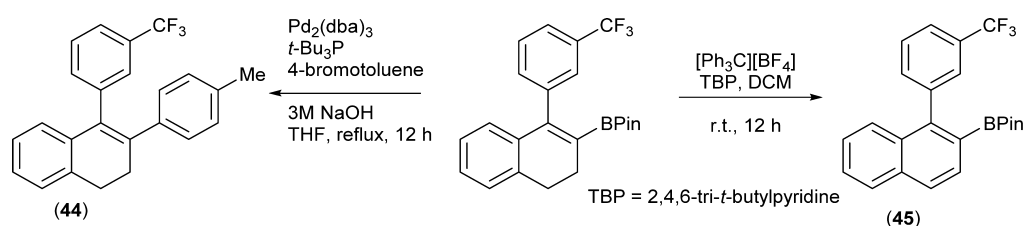
Figure 4. Structures of propargyl esters, amides, ureas, carbonates, and carbamates.

cyclization reaction. Oxazolium salts are seldom reported in the literature and are typically difficult to isolate because of their high reactivity.⁶⁵ In the few reported examples, the dioxoliums have been electronically stabilized through the inclusion of conjugated heteroatoms to delocalize the positive charge.⁶⁶ The products shown in Scheme 29 represent zwitterionic dioxoliums that are able to be isolated and structurally characterized by X-ray crystallography.

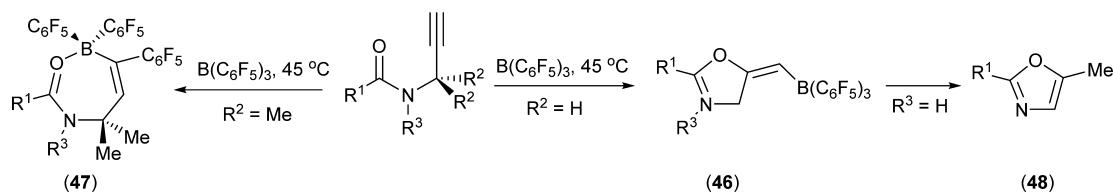
This reactivity was further probed by Melen et al., with the substrate scope extended to terminal propargyl esters, carbonates, and carbamates.⁶⁷ In these cases, a variety of cyclic products were produced and isolated, wherein a 1,1-carboration reaction had occurred, albeit by a different mechanism. The products generated are intramolecularly chelated allylboranes (**50**), as shown in Scheme 30, where the boron is coordinated to the oxygen.

It was also discovered that similar reactivity could be observed with different boron species. Alkyl-, vinyl-, and arylboranes as well as borocations were found to be capable of undergoing migratory group transfer (Figure 5).⁶⁸ The allylboron (**51**) and allylboronium (**52**) products were formed in an atom efficient manner by harnessing the propargyl rearrangement, generally with the selective transfer of a variety of R groups, as shown in Scheme 31. This allowed a novel

Scheme 27. Cross-Coupling and Oxidation of Polycyclic Products



Scheme 28. Cyclizations of Propargylamides



Scheme 29. Cyclization of Propargyl Esters

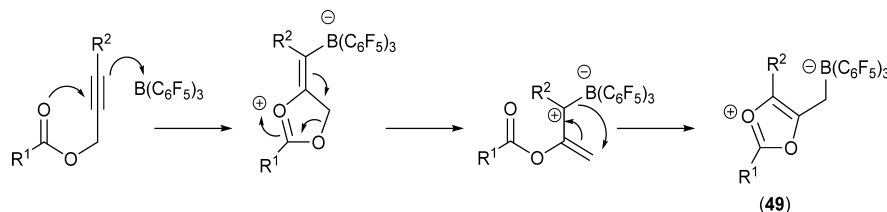
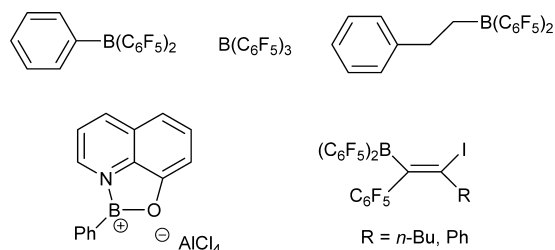
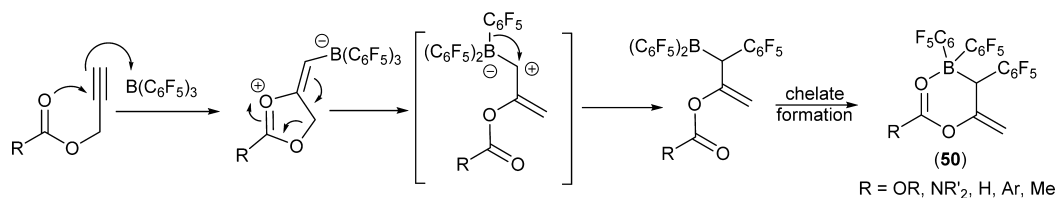
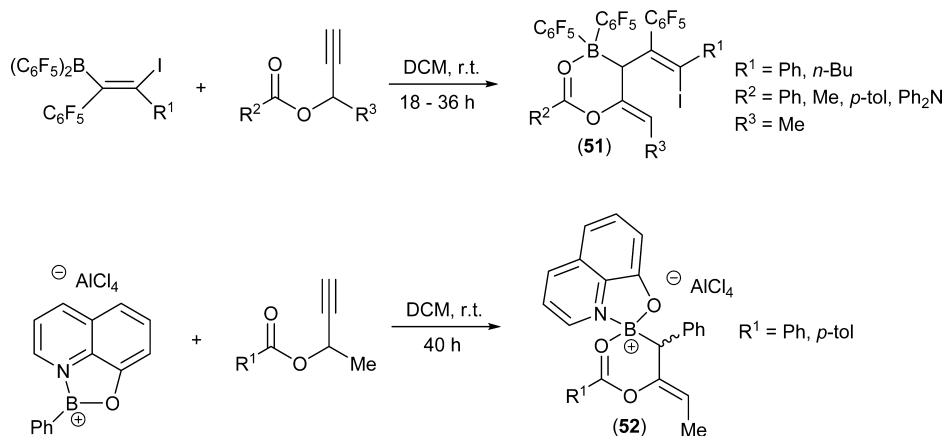
Scheme 30. Propargyl Rearrangement Using $B(C_6F_5)_3$ 

Figure 5. Boranes and borocations used in the propargyl rearrangement.

pathway to access to highly functionalized, synthetically useful cyclic species.

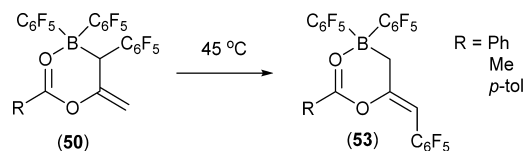
It was also shown that selected allylboron compounds (50), although stable in air and under aqueous conditions, would undergo an irreversible rearrangement when heated to 45 °C.

Scheme 31. Generation of Allylboranes/Borocations from Propargyl Esters



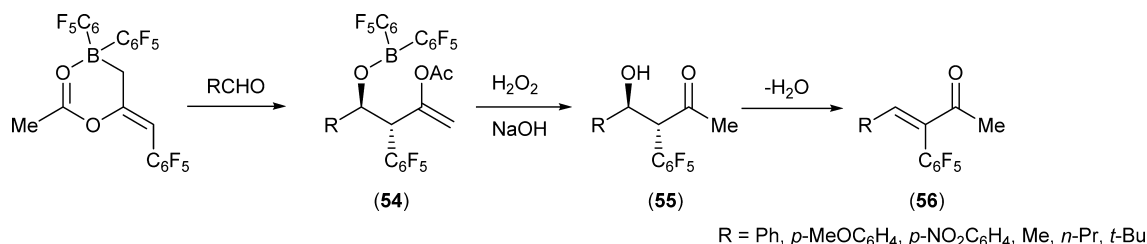
This 1,3-allylboron migration generated the 1,3-carbaboration products (53) featured in Scheme 32, although this rearrange-

Scheme 32. 1,3-Allyl Shift of Allylboron Reagents

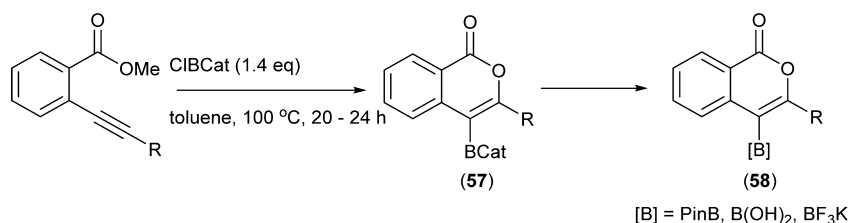


ment was only observed with propargyl esters and $B(C_6F_5)_3$.⁶⁹ It is thought that this rearrangement is similar to the conversion of other allylboranes to the more thermodynamically stable isomers, wherein the boron atom is located on the least-substituted carbon atom and may be further induced by the steric strain of adjacent C_6F_5 groups in 50.⁷⁰

Scheme 33. Reaction of allyl boron compounds with aldehydes



Scheme 34. Synthesis of Borylated Lactones

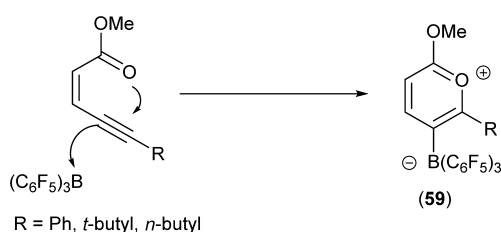


An interesting application of these allylboron compounds was reported alongside the 1,3-rearrangement, namely, their reaction with aldehydes. As shown in Scheme 33, reaction with benzaldehyde generated the allylation product (54) as a single diastereomer. Oxidation with H₂O₂/NaOH generated the β -hydroxy ketone (55), which, during workup, generated the α,β -unsaturated ketone (56). This was extended to a variety of aldehydes to demonstrate the scope of the allylation reaction, which represents a facile route to trisubstituted alkenes with exclusive *E* configuration.

Another example in the growing list of borylative cyclizations is the synthesis of borylated lactones from ester starting materials.⁷¹ It was shown that *trans*-oxyboration of the alkyne moiety occurs in the presence of *B*-chlorocatecholborane without the requisite for a catalyst, only elevated temperature (100 °C). From readily available methyl esters, the borylated isocoumarin (57) and 2-pyrone products were isolated as pinacolboronate esters (58), rendering them useful air-stable synthetic building blocks. The substrate scope for this reaction was shown to include functional groups incompatible with previous borylation techniques.⁷² Esters, cyanides, aryl halides, and thiophenes were all shown to be compatible, providing a diverse range of isolable products (Scheme 34). Similar reactions using B(C₆F₅)₃ with enynoate precursors generated a number of pyrylium borates (59) via a 6-*endo*-dig cyclization, as shown in Scheme 35.⁷³

Following this, a new cyclization reaction was demonstrated, coined as the first formal thioboration reaction.⁷⁴ It was demonstrated that 2-alkynylthioanisoles are suitable for cyclization with *B*-chlorocatecholborane, forming a series of borylated benzothiophenes (Scheme 36). This reaction did not

Scheme 35. Synthesis of Pyrylium Borates



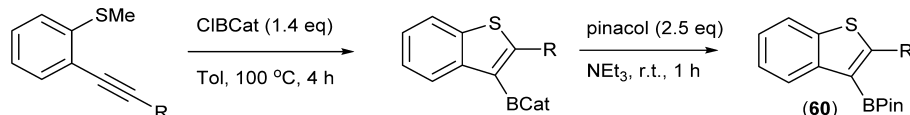
need to be catalyzed, and a range of products were isolated as pinacolboronate esters (60). The proposed mechanistic pathway involves the borane acting as a carbophilic Lewis acid by activating the alkyne bond. The concomitant nucleophilic attack of the sulfur generated a sulfonium intermediate, with subsequent loss of methyl chloride, which, in turn, formed the borylated product.

It was concurrently reported by Ingleson et al. that a similar reaction was possible using BCl₃ and 2-alkynylanisoles to generate borylated benzofurans (61) as pinacolboronate esters.⁷⁵ Reactions were found to proceed readily at ambient temperatures within 1 h, allowing access to a series of borylated products, a selection of which are shown in Scheme 37. The products were presented as viable substrates for cross-coupling reactions, generating synthetically useful 2,3-disubstituted heteroarenes.

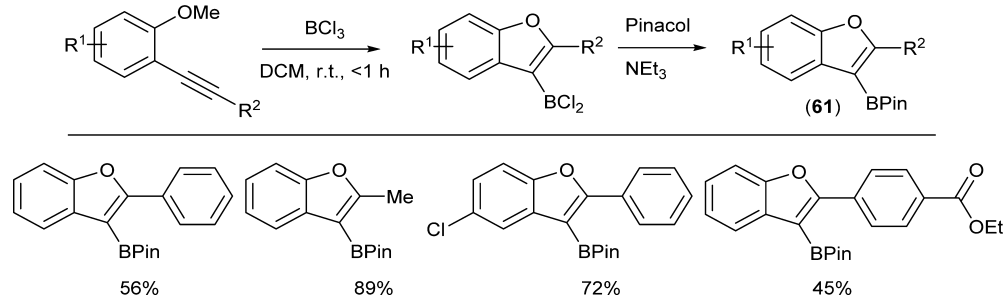
Cyclization of 1,5-enynes to produce functionalized indenenes was found to be possible in a metal-free pathway using B(C₆F₅)₃ as a catalyst as part of an FLP.⁷⁶ The reaction was found to be cycloisomerization, with π activation of the alkyne by B(C₆F₅)₃ and *S-endo*-dig cyclization with the alkene, forming a borylated indene, which undergoes protodeboration, generating 62 (Scheme 38). The use of an FLP system with B(C₆F₅)₃ and Lewis base (PPh₃) was found to be necessary for a catalytic system because the protodeboration step is key to achieving a catalytic turnover. The reactivity was analogous to that reported with transition metals; however, this example highlights the concept that group 13 Lewis acids can act as transition-metal mimics.

The use of boron-based reagents to induce C–C bond formation represents an extremely interesting field of chemistry yielding desirable products. Utilizing the boron reagent to induce cyclization without the need for metal catalysts greatly increases the utility of the product, and further functionalization via cross-coupling reactions at the boron moiety expands the number of cyclic products now available. Several of these reports provide new methodologies to access heterocycles from simple starting materials. Each method has its own advantages, such as gentler reaction conditions or a broader substrate scope. Because heterocycles such as these often possess interesting or useful optoelectronic properties, those that feature sites of

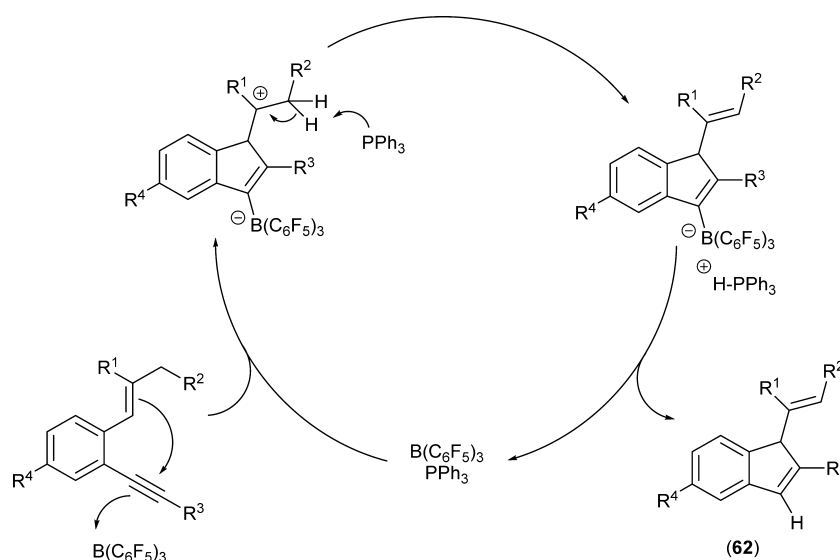
Scheme 36. Thioboration of 2-Alkynylthioanisoles



Scheme 37. Borylative Cyclization of 2-Alkynylanisoles



Scheme 38. Catalytic Cyclization of 1,5-Enynes



functionalization could potentially be modified into monomers for polymerization chemistry.

BORON-CATALYZED HYDROBORATIONS

The hydroboration reaction has been thoroughly explored, with many historic examples using metal catalysts.⁷⁷ More recently, metal-free catalysis has been explored, allowing access to a wider variety of borylated substrates without the necessity of removing trace metal impurities. Many hydroboration reactions are often atom-efficient, utilizing hydroboranes such as pinacolborane (HBPin) with selective addition often observed. Several examples of boron-based catalysts are now present in the literature, select instances of which will now be examined.

Hydroboration of alkenes with HBPin was found to be catalyzed by tris[3,5-bis(trifluoromethyl)phenyl]borane (BAR^{F_3} ; Figure 6), whereas it was found that $\text{B}(\text{C}_6\text{F}_5)_3$ could not be employed.⁷⁸ The reaction generated a series of selective *cis*-1,2-hydroboration products (63) with select examples shown in Scheme 39. The reaction proceeded well on a large substrate scope of substituted styrenes and aliphatic alkenes, with often excellent anti-Markovnikov regioselectivity observed, as is often

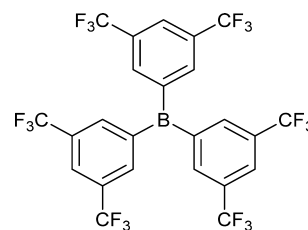
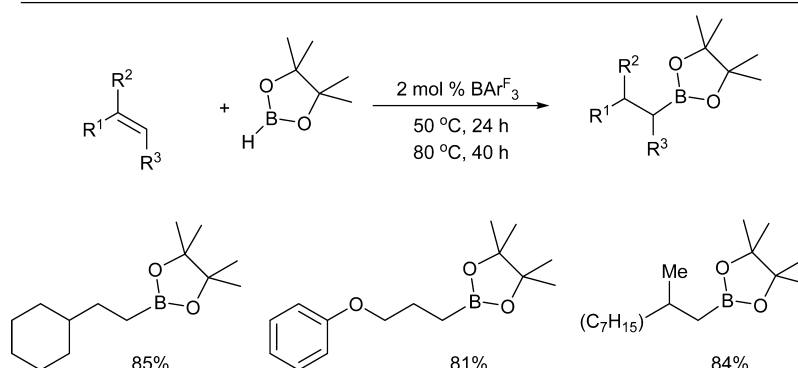
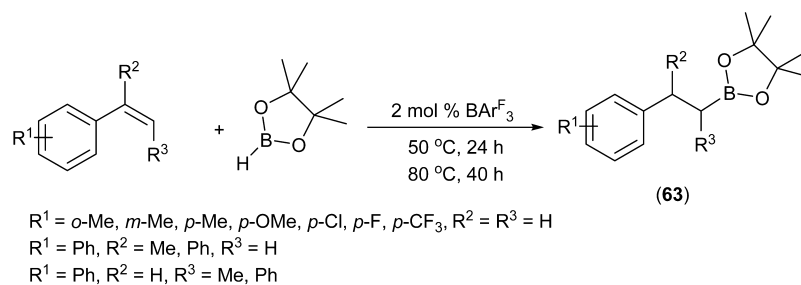


Figure 6. Structure of BAR^{F_3} .

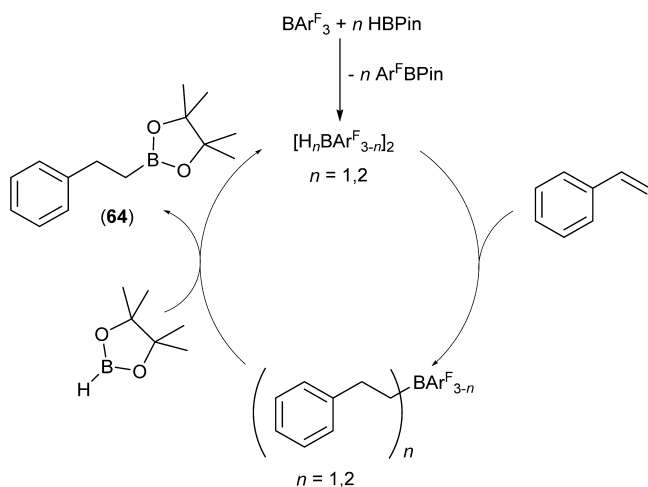
the case with hydroborations because of the hydridic nature of the hydrogen atom.

Following this, the mechanism of the reaction was investigated using stoichiometric control experiments, which found that BAR^{F_3} was actually the precatalyst for the hydroboration of alkenes because it engages in substituent redistribution with HBPin, forming electron-deficient hydroboranes (Scheme 40). It is these species that undergo 1,2-hydroboration of the alkene, followed by ligand exchange with HBPin, generating the pinacolboronate ester product (64) and thus regenerating the catalyst.

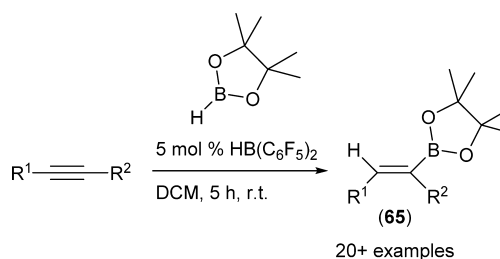
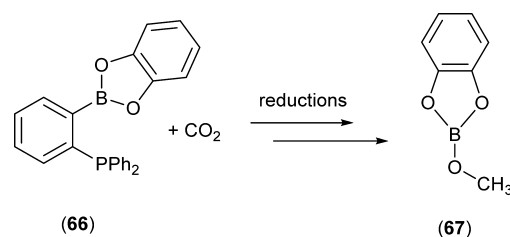
Scheme 39. 1,2-Hydroboration of Styrenes and Aliphatic Alkenes



Scheme 40. Catalytic Cycle for the 1,2-Hydroboration of Alkenes



Scheme 41. 1,2-Hydroboration of Alkynes Using Catalytic Piers Borane

Scheme 42. Hydroboration of CO₂

The catalytic hydroboration of alkynes was reported, wherein Piers borane $[\text{H}-\text{B}(\text{C}_6\text{F}_5)_2]$ was utilized as a catalyst.⁷⁹ Hydroboration gave selectively the (*E*)-vinylpinacolboronate esters (65) and was found to be compatible with a range of terminal and internal alkynes (Scheme 41), although the latter required more aggressive reaction conditions using higher temperatures. When unsymmetrically substituted alkynes were used, a mixture of Markovnikov and anti-Markovnikov products were formed, with the former more prevalent. The Piers borane was found to also act as a precatalyst, in this case generating 1,1-diborylated alkane species in the proposed mechanism.

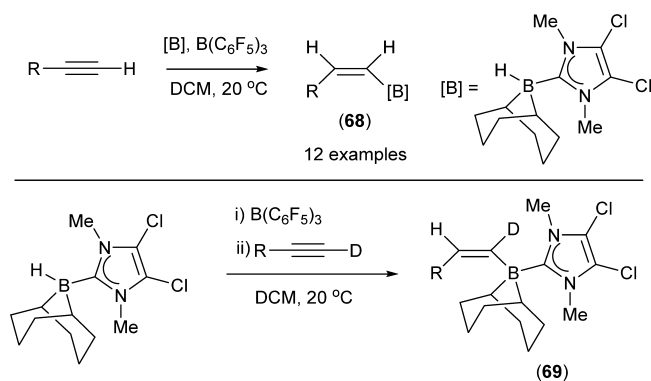
In addition to the hydroboration of C–C bonds, carbonyls and imines as well as CO₂ have been successfully targeted.⁸⁰ Fontaine et al. have demonstrated the hydroboration of CO₂ using a phosphinoborane intramolecular FLP.⁸¹ The catalyst used was the highly ambiphilic 1-catecholbora-2-diphenylphosphabenzene (66; Scheme 42), which was found to be involved

in each step of the reduction of CO₂ to methoxyboranes (67). The full mechanistic pathway and catalytic cycle were determined and proposed as a way to turn a harmful greenhouse gas into a useful fossil fuel substitute.

Ingleson et al. recently reported the metal-free catalytic trans-hydroboration of alkynes using borenium cations and $\text{B}(\text{C}_6\text{F}_5)_3$.⁸² It was found during development of the borenium cation that N-heterocyclic carbenes and chelating dialkyl substituents were necessary to prevent alternative reaction pathways, including dehydroboration. A nonbasic anion was also required to prevent this. A catalytic amount of $\text{B}(\text{C}_6\text{F}_5)_3$ is required to activate the hydroborane precursor to the borenium, which allows for the formation of (*Z*)-alkene products (68; Scheme 43). Deuterium-labeling experiments

established that this was a formal 1,2-trans-hydroboration, as with NMR spectroscopy, confirming the product (69).

Scheme 43. Trans-hydroboration of Alkynes/Deuterium-Labeling Experiments



This selection of modern advances in hydroboration chemistry demonstrates how even a well-established field can be improved upon. Between them, *E*- and *Z*-borylated alkenes and selectively anti-Markovnikov-borylated alkanes can be accessed, in addition to the hydroboration of CO₂, all utilizing boron-based reagents and catalysts. While each of these reports targets different substrates (alkenes, alkynes, and CO₂) using their own tailored reaction conditions and reagents, it is probable that future developments will allow the hydroboration of all of these reagents and more using a singular set of conditions, possibly with novel boron catalysts yet to be unearthed.

CLOSING REMARKS

Although B(C₆F₅)₃ remains a useful and versatile reagent for a range of main-group-mediated transformations, modern advances have demonstrated a need for more specific reagents to allow a tailored approach to reactivity. Through substitution and addition reactions, these new reagents have greatly expanded the ability to install a boron moiety on a greater variety of compounds, allowing access to a wider range of synthetic building blocks. The utilization of these in cross-coupling reactions, with high yields and mild conditions, provides new routes to existing and novel compounds, showing a ubiquitous effectiveness in ligand and drug design, as well as natural product synthesis. In addition, novel boranes and borocations have shown applications in structural transformations, such as additions and cyclizations. These provide a new pathway to synthetically useful cyclic and heterocyclic compounds, and work continues within this area to improve the utility of the boron reagents. Indeed, as the field of boron chemistry advances, a paradigm shift is underway in search of new avenues, pursuing ever more useful transformations using brand new, tailored borane and borocation reagents. It is hoped that, over the next few years, advancements will continue to emerge in this field of chemistry to overcome the remaining challenges. As supplies of traditional metal-based reagents dwindle and prices rise, these main-group reagents and methodologies are poised to become the reactions of choice, providing access to a wide variety of synthetically useful materials.

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Notes

The authors declare no competing financial interest.

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