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Reactions of Allenes with strong Borane-Based Lewis Acids

Urs Gellrich*[a]

In recent years, reactions of unsaturated organic molecules with strong boron-based Lewis acids have attracted considerable attention. In this review, reactions of allenes with boron-based Lewis acids, especially such ones equipped with perfluorophenyl rings, are discussed. It is shown that depending on the substitution pattern of the allene and the borane, a surprisingly broad variety of chemical transformations can be observed.

These transformations often include unexpected skeletal rearrangements of the former allene. Furthermore, some transformations require only catalytic amounts of the borane-based Lewis acid. Within this minireview, emphasis is given to the mechanistic aspects of these transformations, and similarities in the initial reaction steps are outlined.
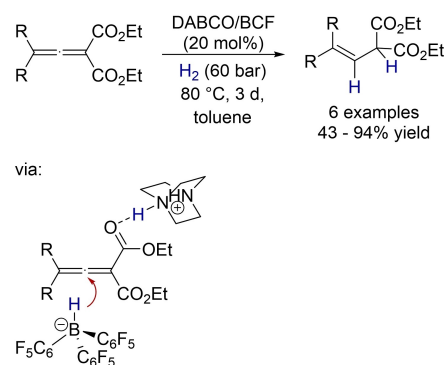
1. Introduction

Boron-based Lewis acids with perfluorinated aryl rings have attracted considerable attention as hydride acceptors in organic synthesis.[1,2] Tris(perfluorophenyl)borane (BCF) is further used as an activator component for homogeneous metallocene–catalyzed Ziegler-Natta olefin polymerization.[3] Furthermore, boron-based Lewis acids are used as part of frustrated Lewis pairs (FLPs), *i.e.* combinations of sterically encumbered Lewis acids and Lewis bases that do not form classic Lewis adducts and are capable of activating strong chemical bonds.[4,5] The FLP-concept led to numerous applications of boron-based Lewis acids in metal-free catalysis, including hydrogenations.[6] Because of their high electrophilicity, boron-based Lewis acids with perfluorinated aryl rings are also able to activate π-bonds and induce interesting transformations of unsaturated organic molecules. One classic example is the 1,1-carboboration of terminal alkynes by tris(perfluorophenyl)borane (BCF) that was discovered independently by the groups of Berke and Erker.[7] Furthermore, Erker and co-workers demonstrated that the 1,1-carboboration of internal alkynes leads to a C—C cleavage, thus a skeletal rearrangement of the alkyne.[8] Within this minireview, reactions of allenes with strong boron-based Lewis acids are discussed. As it is the case for alkynes, repulsion between the π-electrons of the allene renders the double bonds of an allene reactive. However, the presence of the two adjacent double bonds has interesting implications for follow-up reactions of the initial reaction product.

2. Reactions of Allenes with Borane-Based Lewis Acids

This review is organized as follows: First, early examples of the reaction of allenes with strong boron-based Lewis acids are discussed. Secondly, reactions that include hydroborations with electrophilic boranes are summarized. After a brief discussion of the reaction of allenes with haloboranes, the review is closed by describing research achievements regarding the reaction of allenyl ketones and arylallenes with BCF.

2.1. Frustrated Lewis pair-catalyzed hydrogenation of allenes

To broaden the substrate scope for FLP-catalyzed hydrogenations, Alcarazo and co-workers studied the hydrogenation of electron-poor allenes by BCF in combination with different Lewis bases.[9] They found a superior reactivity of amine Lewis bases compared to phosphines such as tri-*tert*-butylphosphine and tri-mesitylphosphine for the hydrogenation of ester-substituted allenes. With an FLP-catalyst composed of 1,4-diazabicyclo[2,2,2]octane (DABCO) and BCF, six different ester substituted allenes were successfully hydrogenated (Scheme 1). The authors propose a mechanism that commences with H_2

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Scheme 1. The hydrogenation of electron-poor ester substituted allenes by an FLP and the postulated 1,4-hydride transfer (DABCO = 1,4-diazabicyclo[2,2,2]octane; BCF = tris(perfluorophenyl)borane).

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activation by the FLP. The protonated amine activates then the electron-poor allene by a hydrogen bond to the ester group (Scheme 1). This interaction enables a 1,4-addition of the hydride mediated by the borohydride that was formed in course of the H_2 activation. This mechanistic scenario is supported by deuteration experiments.
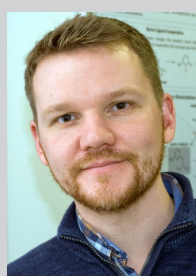
Remarkably, the hydrogenation of tetraphenylallene **1** under similar conditions leads to a mixture of products. Aside from the reduced species **2**, the indene **3** was observed (Scheme 2). It is assumed that the indene is formed by the addition of the central carbon of the allene to the BCF, followed by Friedel-Crafts alkylation of one of the phenyl rings. This hypothesis is supported by the finding that allene **4** undergoes a clean cyclization to the indene **5** in the presence of catalytic amounts of BCF. The addition of the allene to BCF leads in both cases to a zwitterion in which the positive charge is resonance stabilized and in a benzylic position.

The formation of the indenes observed in this research project gives a first hint on the versatile reactivity of allenes with strong boron-based Lewis acids.
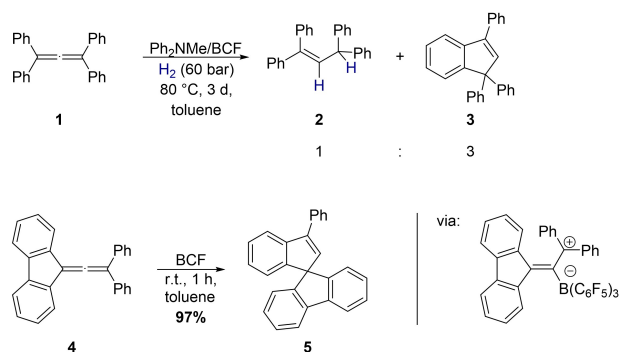
2.2. Reactions initiated by the hydroboration of allenes by electrophilic boranes

Hydroboration of double or triple bonds by Piers' borane ($HB(C_6F_5)_2$, **6**) is a convenient way to introduce $B(C_6F_5)_2$ groups into an organic molecule and was frequently used for the synthesis of intramolecular FLPs. One example is the hydroboration of the dimesitylphosphanylallene **7** by Piers' borane **6** that yields **8** (Scheme 3).[10] However, regarding bond activation **8** does not display the typical FLP reactivity.

Notably, the reaction of Piers' borane **6** with an excess of unsubstituted allene did not furnish the product of a simple hydroboration, but rather the borane substituted trimer **9** (Scheme 4).[11] Upon a prolonged reaction time, retro-hydroboration and the formation of the symmetric trimer **10** were observed. The initial product **9** can be captured as the Lewis base adduct **11** upon addition of *N,N*-bis-(mesityl) imidazolylidene (IMes) or, upon addition of pivaloylnitrile, as the Lewis adduct **12**. Both adducts were fully characterized, including SCXRD (single crystal X-ray diffraction) analysis.

Scheme 2. Formation of the indenes **3** and **5** upon cyclization of an allene, induced by BCF (BCF = tris(perfluorophenyl)borane).
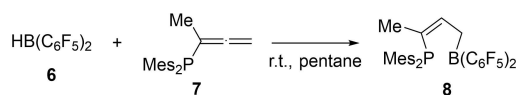
Scheme 3. Formation of the FLP **8** upon hydroboration of dimesitylphopha-nylallene **7**.

Scheme 4. a) Formation of the allene trimers **9** and **10** upon the reaction of allene with Piers' borane **6** and b) follow-up reactions of **9**.
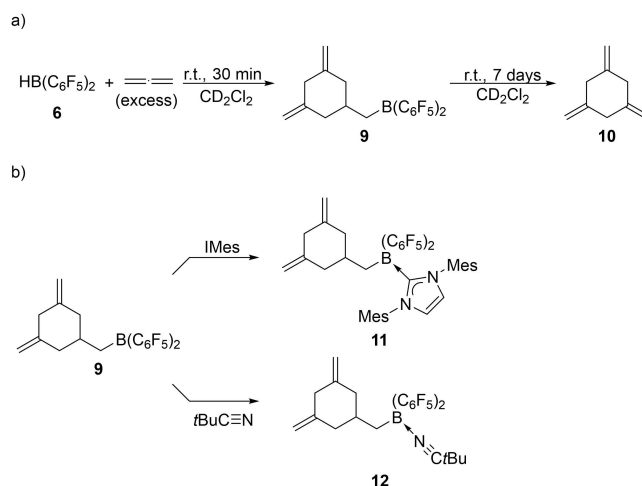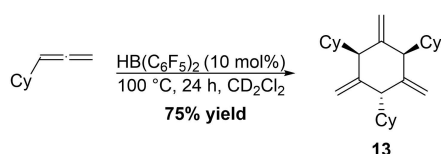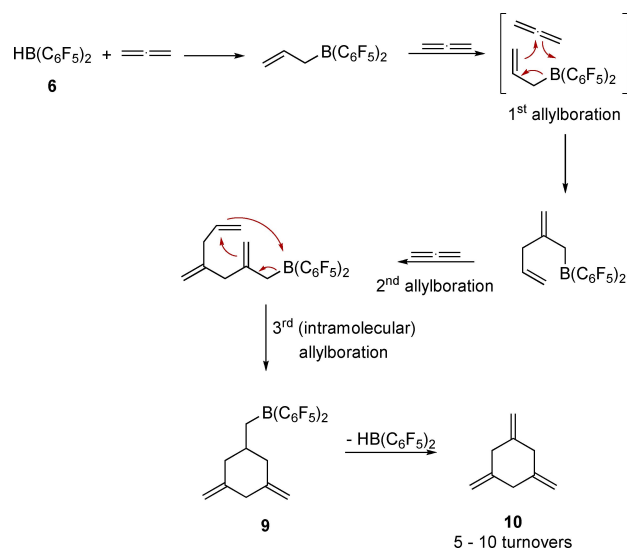
Urs Gellrich studied chemistry at the University of Freiburg in Germany where he obtained his Doctorate in 2013 for his work on supramolecular ligands under the guidance of Prof. Bernhard Breit. He then joined the group of Prof. David Milstein at the Weizmann Institute of Science as PostDoc. In 2017 Urs started his independent career as a Liebig Fellow of the FCI at the Justus Liebig University Giessen where he is currently Emmy Noether Group Leader. His research focuses on the **in silico** design of novel metal-free systems for bond activation and catalysis.

The retro-hydroboration of **9** regenerates Piers' borane which indicates that a catalytic trimerization is possible. Indeed, the reaction of cyclohexylallene with catalytic amounts of Piers' borane **6** yielded the trimer **13** in good yields as a single stereoisomer with a *cis,trans*-arrangement of the cyclohexyl substituents at the carbocyclic core (Scheme 5). This reaction is a rare example of a catalytic, transition metal-free allene trimerization.

The proposed mechanism of the cyclotrimerization of allenes consists of a series of allylborations (Scheme 6). The allylborane formed from the initial hydroboration of allene reacts with a second equivalent of allene to form a new allylborane. A second allylboration of a third equivalent of allene and an intramolecular allylboration leads then to the

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Scheme 5. Cyclotrimerization of cyclohexylallene catalyzed by Piers' borane **6**.

Scheme 6. Proposed mechanism for the trimerization of allenes catalyzed by Piers' borane **6**.

Scheme 7. Piers' borane mediated cyclization of oligo methylene linked bis-allenes via an intramolecular allylation.

Scheme 8. 1,2-Addition of triphenylphosphine and the B(C₆F₅)₂ fragment to the double bond of **15a**. Conditions: r.t., CD₂Cl₂.

Scheme 9. Formation of the bicyclic borane **19a** upon the reaction of **15a** with an excess of allene (dr = diastereomeric ratio).

formation of the trimer **9**. As mentioned, a retro-hydroboration yields **10** and regenerates Piers' borane **6**. The mechanistic proposal is supported by deuteration experiments using DB-(C₆F₅)₂. However, at this stage, it remains unclear if the initial allylborations take place in an intermolecular fashion or if the coordination of the allene to the Lewis acidic borane precedes an intramolecular allylation via a six-membered transition state.
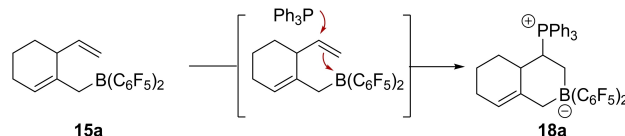
The hydroboration of the trimethylene-linked bis-allene **14a** and the tetramethylene linked bis-allene **14b** by Piers' borane **6** enabled an intramolecular allylboration that leads to a ring-closure and formation of the boranes **15a** and **15b** (Scheme 7).[12] Likewise, a hydroboration of the phenyl-bridged bis-allene **16** followed by an intramolecular allylboration lead to the formation of the bicyclic borane **17**.

All three products (**15a**, **15b**, and **17**) were successfully isolated as their respective pyridine adducts. Furthermore, the presence of a vinylic group in proximity to the sterically encumbered Lewis acidic borane allows for a 1,2-borane-phosphine addition. This reaction is exemplified in Scheme 8 for **15a**.
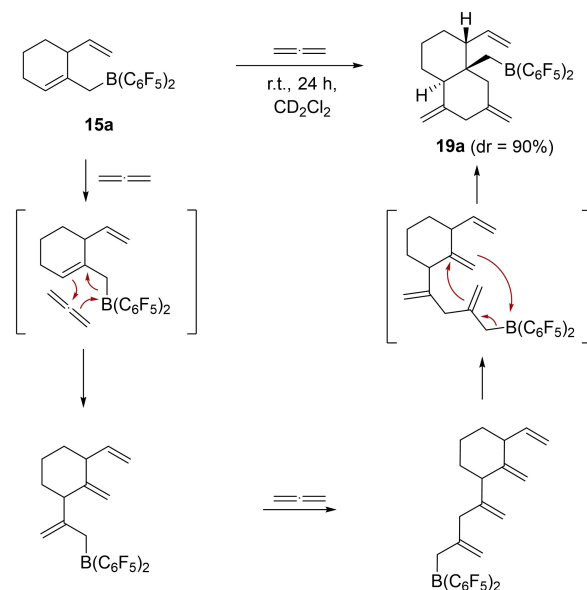
The compounds **15a** and **15b** both contain an allylborane fragment. To investigate if this allylborane fragment can be engaged in further allylations, Erker and co-workers exposed **15a** to an excess of allene.[12] This led to the formation of the bicyclic borane **19a** with high diastereoselectivity (Scheme 9). The formation of **19a** is assumed to commence with the

allylboration of allene by **15a**. The product of this reaction is again an allylborane that reacts with a second equivalent allene. The intermediate formed by the second allylboration then

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underwent an intramolecular allylboration that led to a favorable 6-*exo-trig* cyclization.

Interestingly, the reaction of Piers' borane **6** with arylallenes **20** takes a different course.[13] In this case, dimerization, and the formation of the boryl substituted 1,6-diaryl-1,5-hexadiens **21a**–**21d** was observed (Scheme 10).

NMR investigations showed that the reaction of Piers' borane **6** with one equivalent phenylallene yields allylborane **22** (Scheme 11a). The addition of one additional equivalent phenylallene leads to the formation of diene **23** within minutes. Again, this reaction can be described as an allylboration of the phenylallene. A Cope rearrangement then yields the final product **21a**. The Cope rearrangement is slow compared to the formation of **23**. However, it is remarkable that this reaction takes place at r.t. as Cope rearrangements of structurally similar dienes usually require temperatures of about 100 °C.[14] This indicates that the electrophilic boryl substituent facilitates the rearrangement. Intermediate **23** was captured as Lewis adduct by the addition of phosphines and pyridines and structurally characterized by SCXRD. The diene **21a** was successfully used in a Suzuki-Miyaura coupling with 4-iodotoluene that gave
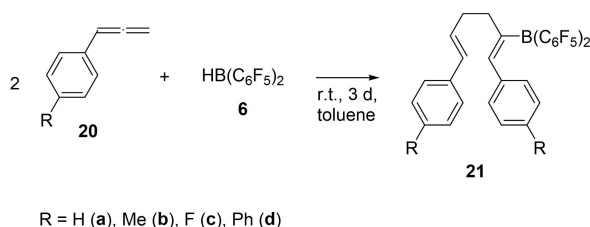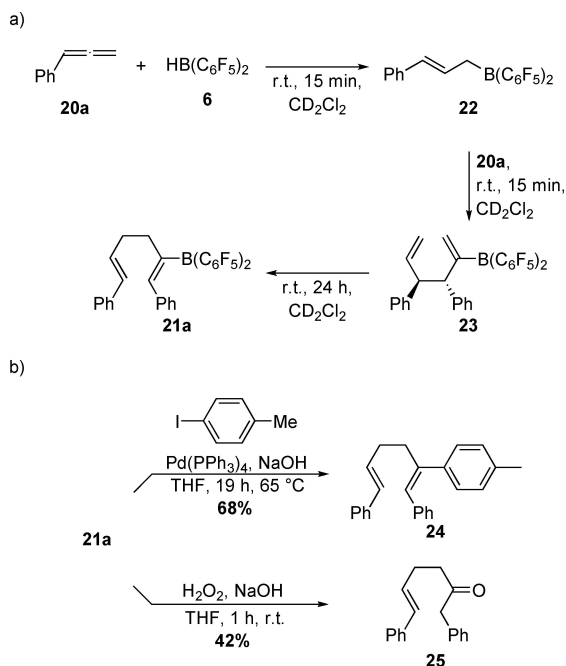
triarylhexadiene **24** (Scheme 11b). Treatment of **21a** with hydrogen peroxide under basic conditions leads to oxidative cleavage of the C–B bond and furnished ketone **25** (Scheme 11b). These reactions demonstrate the synthetic utility of borane **21a**.

We recently reported H_2 activation by the pyridonate borane-based FLP **26**.[15] A distinctive feature of this FLP is that the covalently bound pyridonate substituent changes to a datively bound pyridone ligand. Thus, the pyridone borane complex **27**, which is formed upon hydrogen activation, can dissociate into the pyridone **28** and Piers' borane **6**. We exploited this reactivity for the formation of the allylborane pyridone complex **29** from phenylallene **20a** and H_2 (Scheme 12). The key step of the formation of **29** is the hydroboration of phenylallene **20a** by Piers' borane **6**.[16]

To prove that an allylborane generated in this way is nucleophilic, **26** was reacted with phenylallene **20a** and acetonitrile as electrophile under a hydrogen atmosphere. However, this reaction did not lead to the expected formation of an allylimine but rather to the formation of the β-diketiminate borane complex **30** and the bispyridone complex **31** (Scheme 13a). NMR investigations and DFT computations indicate that the formation of **30** commences with the reaction sequence of hydrogen activation by the pyridonate borane **26** and the subsequent hydroboration of phenylallene that is shown in Scheme 12. The allylborane **22** then allylates acetonitrile to give the ketiminoborane **32** (Scheme 13b). The allylimine borane complex **33** that is formed upon coordination of pyridone **28** was identified and characterized by NMR spectroscopy. We assume that the pyridone **28** mediates the tautomerization of the allylimine to an enamine. This enamine reacts then with a second equivalent acetonitrile in a 1,2-addition that yields **30**.

R = H (**a**), Me (**b**), F (**c**), Ph (**d**)

Scheme 10. Dimerization of arylallenes induced by Piers' borane.

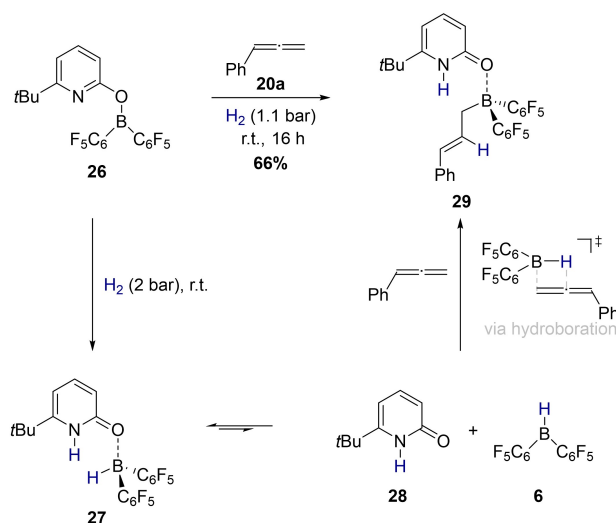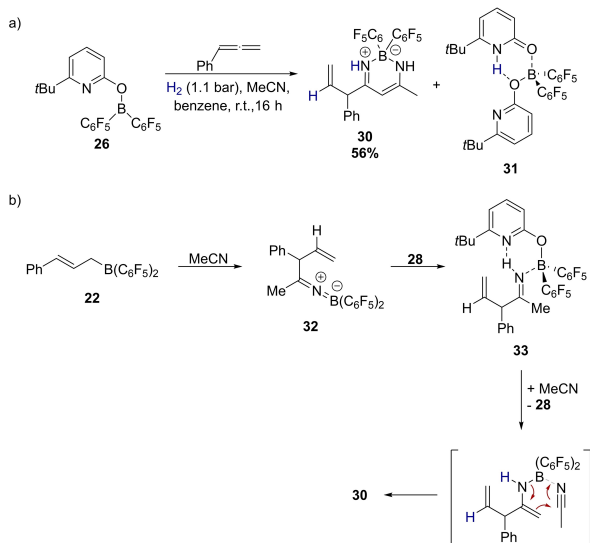**Scheme 11.** Stepwise formation of diene **21a** via a sequence of allylboration and Cope rearrangement.

Scheme 12. Formation of the allylborane **29** by a reaction sequence consisting of hydrogen activation by **26**, dissociation of the pyridone borane complex **27**, hydroboration of phenylallene **20a**, and re-coordination of pyridone **28**.
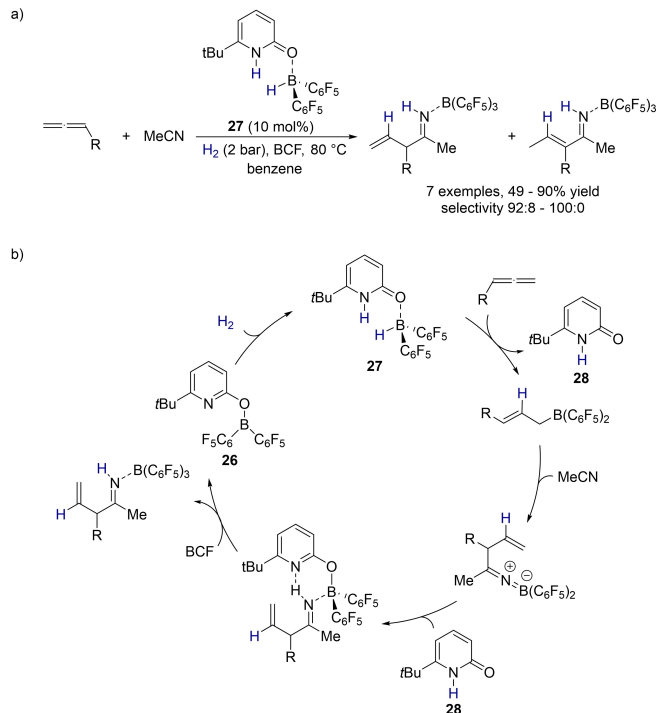
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Scheme 13. a) Formation of the β-diketiminate borane complex **30** upon the reaction of the pyridonate borane complex **26** with phenylallene, acetonitrile, and hydrogen. b) Reaction sequence consisting of the allylation of acetonitrile, the tautomerization of the allylimine, and a 1,2-addition to a second equivalent of acetonitrile.

Scheme 14. a) Allylation of nitriles by an allylborane formed *in situ* from H₂ and an allene. Selectivity refers to the ratio of allylimine and vinylimine. b) The proposed cycle for the allylation of nitriles catalyzed by **26** in the presence of BCF (BCF = tris(perfluorophenyl)borane).

While this experiment proves that **22** is indeed a competent nucleophile for the allylation of nitriles, the irreversible formation of β-diketiminate borane complex **30** inhibits further catalytic reactivity. Therefore, we added BCF to capture the allylimine before the 1,2-addition as Lewis adduct. Removal of the allylimine from complex **33** was further assumed to regenerate the pyridonate borane complex **26** as the active catalyst for the hydrogen activation. Indeed, using stoichiometric amounts of BCF, we were able to develop a catalytic allylation of nitriles from allenes and dihydrogen with only 10 mol% of **26** as the active catalyst (Scheme 14). The proposed mechanism, which consists of the elementary steps discussed in this section, is summarized in Scheme 14.

2.3. Reactions initiated by the haloboration of allenes by electrophilic boranes

Inspired by the finding that Piers' borane **6** catalyzes the cyclotrimerization of allenes, Erker and co-workers probed the reaction of allene with the electrophilic haloboranes ClB(C₆F₅)₂ **34a** and BrB(C₆F₅)₂ **34b**.[17] The reaction leads to the formation of the trimer **10** and the haloborylated tetramer **35a** and **35b** in a 1:1 and 1:2 ratio, respectively (Scheme 15). Presumably, **10** is formed in a reaction sequence that is analogous to that of allene with Piers' borane **6**. The tetramers **35a** and **35b** originate then from an allylboration of a fourth equivalent allene prior to the cyclization.
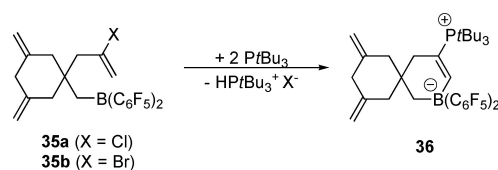
The tetramers **35a** and **35b** display the reactivity of Lewis acids and react with the bulky Lewis base P*t*Bu₃ in ring closure reaction that yields the spirocyclic compound **36** (Scheme 16). This reaction is likely initiated by a 1,2-borane phosphine
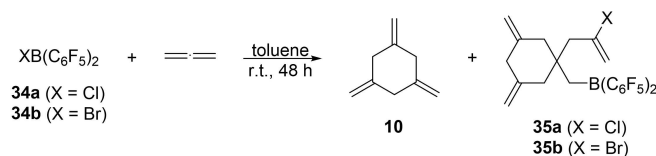
Scheme 15. Formation of the allene trimer **10** and the haloborylated allene tetramers **35a** and **35b**.

Scheme 16. Formation of **36** upon the reaction of the haloborylated allene tetramer **35a** and **35b** with P*t*Bu₃. Conditions: toluene, 24 h, r.t.

addition to the double bond of **35** (see Scheme 8), followed by an elimination of HX.

Furthermore, the haloboranes **34a** and **34b** catalyze the trimerization of **n**-dodecylallene. Given the similarity in the reactivity of the haloboranes **35a** and **35b** with Piers' borane towards alkylallenes, one would expect that a similar reactivity could also be observed towards arylallenes. However, this is not the case. While Piers' borane **6** induces the dimerization of arylallenes (see Scheme 10), the reaction of the haloboranes
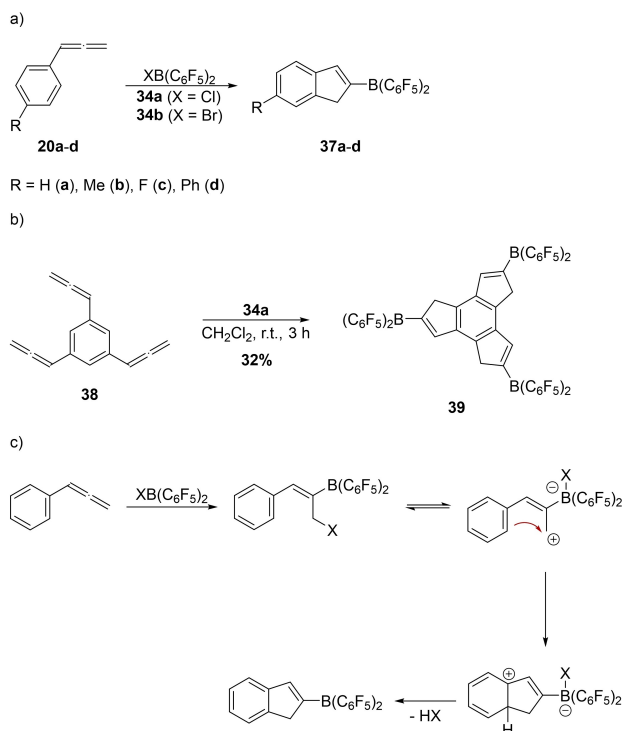
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34a and **34b** with arylallenes yields 2-borylindenes **37** (Scheme 17a).[18] This reaction was also used for the three-fold cyclization of **38** that yielded the triindene **39**.

This divergence in reactivity is rationalized by a mechanistic proposal for the reaction of arylallenes with haloboranes that commences with the haloboration of the terminal double bond. Ionization of the allylic halide formed by this reaction enables the cyclization of the former arylallene via an intramolecular Friedel-Crafts alkylation (Scheme 17b). This reaction was extended to bis- and trisallenylbenzene.
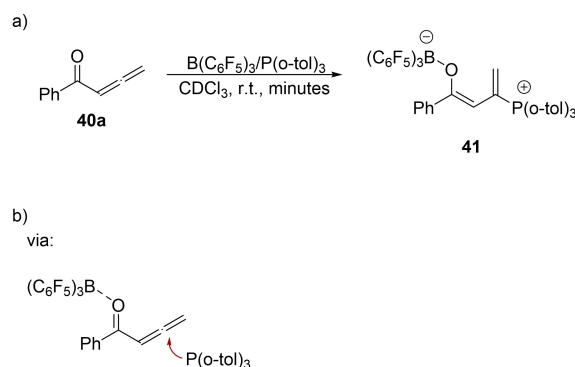
2.4. Reactions of allenyl ketones and arylallenes with BCF

In 2015, Melen *et al.* reported a study addressing the reactivity of phosphine-BCF FLPs towards allenyl ketones.[19] They observed a 1,4-type addition of the FLP to the allenyl ketone, which is according to the mechanistic proposal initiated by activation of the allenyl ketone by BCF, followed by the nucleophilic addition of the phosphine to the central carbon of the allenyl moiety. A typical example is the reaction of the allenyl arylketone **40a** with an FLP containing BCF and tris (*ortho*-tolyl)phosphine that yields the zwitterion **41** (Scheme 18).
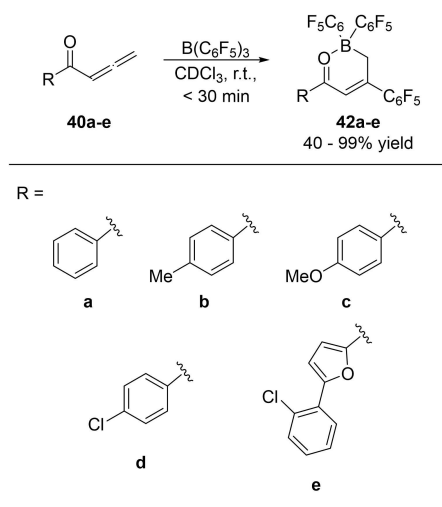
Remarkably, the reaction of the allenyl ketones with BCF in the absence of a Lewis base yielded the borane substituted α,β-unsaturated ketones **42a–e** (Scheme 19). Thus, the BCF underwent a formal 1,2-carboboration with the allenyl ketones.

Scheme 18. Addition of phosphine-BCF containing FLPs to allenyl ketones.

Scheme 19. Formal 1,2-addition of BCF to the terminal double bond of allenyl ketone.

Scheme 17. The reaction of arylallenes with the haloboranes **34a** and **34b** yields 2-borylindenes. Conditions (unless otherwise stated): CD$_2$Cl$_2$, 5 min, r.t.

According to the mechanistic proposal, this reaction is initiated by the coordination of the BCF to the carbonyl oxygen of the allenyl ketone (Scheme 20). This coordination imposes a positive partial charge on the central carbon of the allene moiety and precedes a 1,5-sigmatropic shift of one C$_6$F$_5$ group. The product of this rearrangement can be described as a vinylogous enol ether and attacks the B(C$_6$F$_5$)$_2$ in an intramolecular reaction that leads to the ring closure and the formation of **42**.

The reaction of allenyl ester **43** with BCF in the presence of water leads to a different outcome. In this case, the formation of the γ-lactone cyclization product **44** was observed (Scheme 21). This reaction presumably commences with the activation of the π-system by BCF that enables a nucleophilic attack of the ester group on the terminal carbon of the allene. Water effects the hydrolysis of the ester group.

The coordination of the carbonyl oxygen to BCF is stronger in the case of allenyl ketones than in the case of allenyl esters. Thus, alternative pathways that include the activation of the π-system of the allene become accessible in the latter case. We recently reported that the reaction of phenylallene **20a** with

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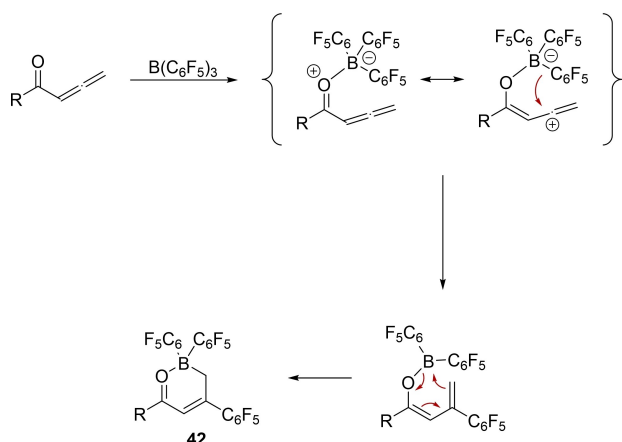
Scheme 20. Proposed mechanism for the formation of borane substituted α,β-unsaturated ketones **42** upon the reaction of BCF with allenyl ketones.
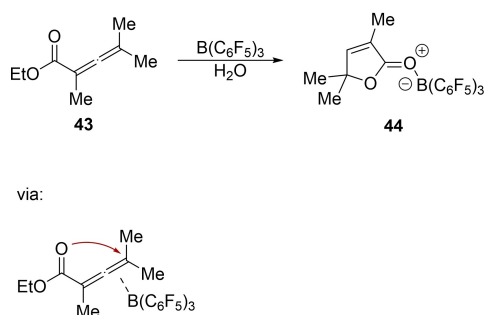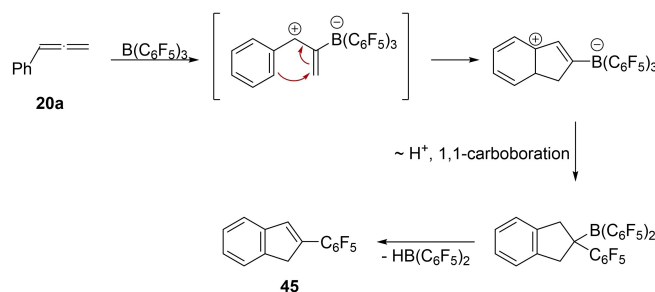
Scheme 21. Formation of the BCF-coordinated lactone **44** upon the reaction of allenyl ester **43** with BCF and the activation of the π-system of **43** by BCF. Conditions: toluene, 72 h, r.t.
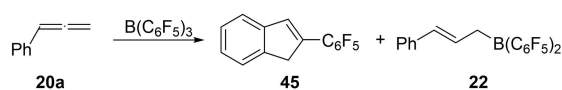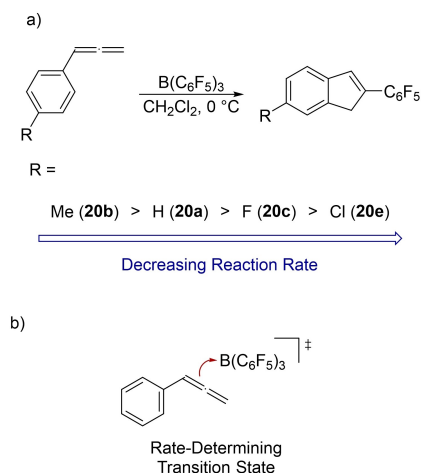
Scheme 22. Formation of indene **45** upon the reaction of phenylallene **20a** with BCF. Conditions: CH₂Cl₂, 45 min, r.t.

Scheme 23. Proposed mechanism for the formation of indene **45**.

Scheme 24. a) Summary of the Hammett Plot analysis for the BCF induced formation of pentafluorophenyl substituted indenes from aryl allenes and b) the rate-determining transition state identified by DFT computations.

BCF yields pentafluorophenyl substituted indene **45** (Scheme 22).[20] As a side product of this reaction, allylborane **22** was observed, indicating that Piers' borane **6** is formed as an intermediate during the reaction.

The transfer of the pentafluorophenyl ring and the intermediate formation of Piers borane hint at a mechanism that includes a 1,1-carboboration as C–C bond-forming step and a retro-hydroboration. Therefore, we proposed a mechanism that commences with the addition of the central carbon of the allene to the BCF yielding a resonance stabilized zwitterion (Scheme 23). Note that this step is analogous to the one proposed by Alcarazo and co-workers as the initial step of the formation of indene **5** (see Scheme 2). An intramolecular Friedel-Crafts alkylation leads to ring closure and formation of the indene core. A reaction sequence of proton-migration, 1,1,-

carboboration and retro-hydroboration yields then indene **45** and liberates Piers' borane **6**.

A Hammett plot analysis of the BCF induced formation of pentafluorophenyl aryl allenes revealed a negative slope, *i.e.* electron-donating substituents in the para-position of the phenyl ring accelerate the reaction while electron-withdrawing groups in this position slow down the reaction (Scheme 24). This finding indicates that a positive partial charge is build up in the benzylic position in the rate-determining transition state of this reaction. Indeed, DFT computations indicate the initial addition of the allene to the BCF to be rate determining.

3. Conclusion and Outlook

As shown in this minireview, the reaction of allenes with strong boron-based Lewis acids can lead to a plethora of chemical transformations. Many of these transformations include a carbon-carbon bond formation and are thus of synthetic relevance. Some of the transformations that are discussed in this review are catalytic with respect to the borane-based Lewis acid and are thus relevant to main-group catalysis. Furthermore, it was shown that the products that contain a boryl side can be engaged in Suzuki-Miyaura type coupling reactions. That opens

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the possibility to use these reactions for the synthesis of complex boranes that are difficult to prepare by classic methods as substrates for transition-metal catalyzed coupling reactions. We expect to see more detailed mechanistic investigations and applications in synthetic chemistry of the transformations discussed in this review in the upcoming years.

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Conflict of Interest

The authors declare no conflict of interest.

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