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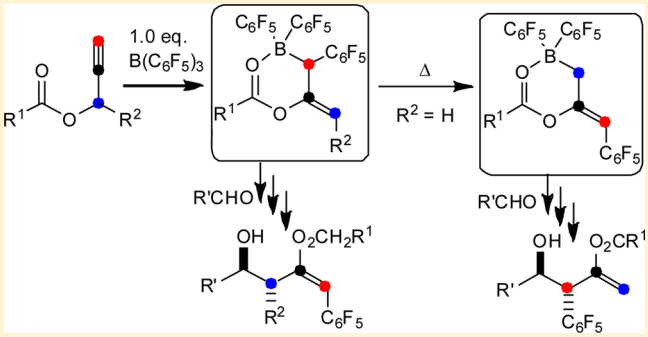
Activation of Alkynes with $B(C_6F_5)_3$ – Boron Allylation Reagents Derived from Propargyl Esters

Max M. Hansmann,[†,§] Rebecca L. Melen,[‡,§] Frank Rominger,[†] A. Stephen K. Hashmi,*[,†] and Douglas W. Stephan*[,‡]

[†]Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
[‡]Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada
[§]Chemistry Department, Faculty of Science, King Abdulaziz University (KAU), Jeddah 21589, Saudi Arabia

Supporting Information

ABSTRACT: Novel allyl boron compounds are readily synthesized via rearrangement reactions between Lewis acidic $B(C_6F_5)_3$ and propargyl esters. These reactions proceed through an initial cyclization followed by ring-opening and concurrent C_6F_5-group migration. In the absence of disubstitution adjacent to the ester oxygen atom, an allyl boron migration rearrangement leads to formal 1,3-carboboration products. These allyl boron compounds act as allylation reagents with aldehydes introducing both a C_3-allyl fragment and a C_6F_5-unit as a single *anti*-diastereomer. In these reactions, $B(C_6F_5)_3$ activates the alkynes, prompting the rearrangement processes and enabling installations of C_6F_5 and R-groups.

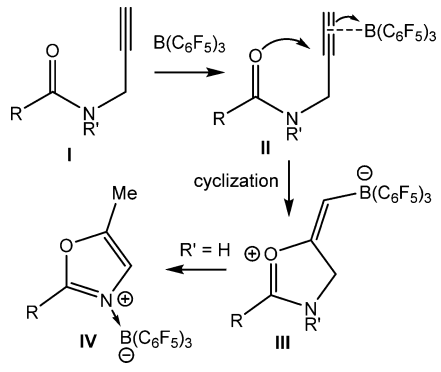


INTRODUCTION

Allylation and crotylation reactions have gained a prominent position as tools in organic synthesis for the construction of carbon−carbon bonds.[1] Traditionally, η^1-allyl-transfer reagents are derived from main group compounds such as allylboron,[2] allylsilane,[3] or allylstannanes.[4] The allyl or crotyl-boron reagents are generally less toxic and more reactive than the silicon and tin counterparts. The allyl additions of organoboron reagents to carbonyl compounds are highly diastereoselective and enantioselective when chiral boranes are employed. These reagents have found widespread applications in organic chemistry and natural product synthesis.[5] Synthetic routes to such boron allylation reagents include hydroboration, transition metal-catalyzed borylation of allylic compounds with bis-(pinacolato)diboron, or the addition of reactive allyl lithium, allyl magnesium, and allyl potassium reagents to a borinic or boric ester.[6]

The Lewis acid $B(C_6F_5)_3$ was first reported in the 1960s[7] and has found widespread applications in organometallic and organic chemistry,[8,9] olefin polymerization,[10] and hydrosilylation.[11] In recent years, $B(C_6F_5)_3$ has been exploited as the Lewis acid component in frustrated Lewis pair (FLP) chemistry.[12] FLPs, first described in 2006,[13] consist of Lewis acids and bases that act in concert to activate a wide range of small molecules or to effect catalysis.[12] For example, suitable combinations of Lewis bases (including amines,[14] phosphines,[15] amides,[16] and pyrroles[17]) and $B(C_6F_5)_3$ undergo 1,2-addition reactions to C−C π-bonds of olefins or alkynes. We have previously reported analogous intramolecular reactions of propargyl amides with the Lewis acid $B(C_6F_5)_3$,[16] which afford stable zwitterionic 5-alkylidene-4,5-dihydrooxazolium borate species (**III**) via an intramolecular 5-*exo* oxyboration reaction. This can, in some cases (R′ = H), aromatize to afford oxazole products (**IV**) (Scheme 1).[16] Herein, we exploit this initial π-activation mode to uncover a novel synthetic route to functionalized boron allylation reagents from propargyl esters. These reagents are subsequently utilized as allylation reagents

Scheme 1. Cyclization Pathways of Propargyl Amides with the π-Lewis Acid $B(C_6F_5)_3$



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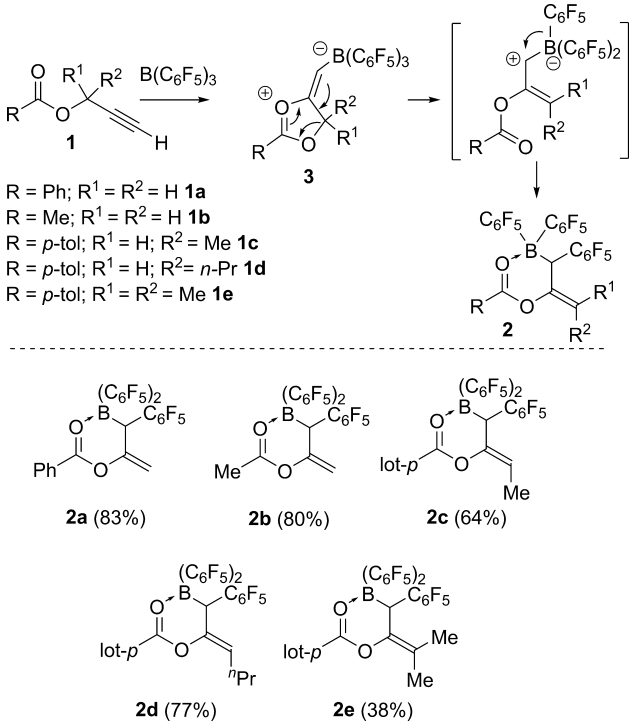
with aldehydes enabling the installation of C_6F_5 and R-groups, opening a new route to highly functionalized organic compounds.

RESULTS AND DISCUSSION

The 1:1 stoichiometric reaction of the propargyl ester **1a** with $B(C_6F_5)_3$ in CH_2Cl_2 at 45 °C results in the rapid and clean formation of the cyclic allyl boron compound **2a** (Scheme 2) in

Scheme 2. Synthesis of Allyl Boron Reagents via a Propargyl Rearrangement[a]



[a]Isolated yields are indicated.

which C_6F_5-group migration from boron to carbon has occurred. It is noteworthy that direct 1,1-carboboration of terminal alkynes is known to afford vinyl-boranes;[18] this is not seen in the case of the present reactions, as the propargyl rearrangement process is significant faster.

This reaction between **1a** and $B(C_6F_5)_3$ was found to be strongly solvent dependent with no evidence of reaction in coordinating solvents such as d_8-THF or d_3-MeCN. Nonetheless, the reaction was rapid and clean in CD_2Cl_2 and slower in d_8-toluene, d_6-benzene, and d_5-bromobenzene. The analogous reactions of **1b–e** with $B(C_6F_5)_3$ afforded the corresponding compounds **2b–e** in high conversions and yields. The reactions of **1c** and **1d** were particularly rapid giving the allyl boron compounds **2c** and **2d** in less than 15 min at room temperature. These cyclizations are much faster than those previously described for propargyl amides,[16] presumably a result of poorer coordination ability of the ester carbonyl in comparison to the propargyl amide fragment,[19] enabling faster π-alkyne activation. These stoichiometric reactions were scaled up to afford the products **2a–e** in good to high yields (in most cases quantitative by in situ NMR), which were fully characterized by ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectroscopy. In the case of compounds **2c** and **2d**, the *Z*-isomer was exclusively formed. X-ray crystallography was also used to characterize **2a**, **2c**, **2d**, and **2e** (Figure 1 and Supporting Information), which exhibited similar geometric parameters. X-ray diffraction analysis also

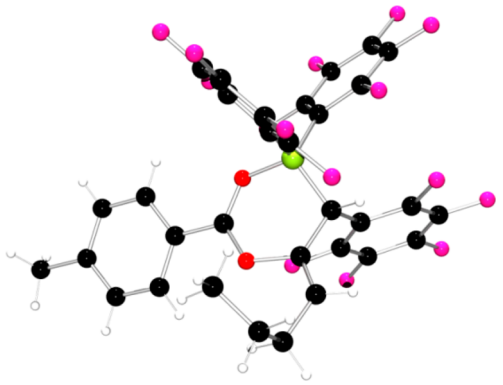


Figure 1. POV-ray depictions of the molecular structure of **2d**. C, black; O, red; F, pink; B, yellow-green. Analogous structures of **2a**, **2c**, and **2e** are deposited in the Supporting Information.

confirmed the *Z*-configuration about the C=C double bond in **2c** and **2d**. Efforts to employ other boranes (including BPh_3 and $BF_3{\cdot}OEt_2$) in this rearrangement reaction gave no conversion even at elevated temperatures (50 °C) for 24 h.

These reactions are thought to proceed via a reactive zwitterionic intermediate (**3**) (Scheme 2), which rapidly rearranges to yield compounds of type **2** by a C_6F_5 group migration. This migration is enabled as a result of the carboxylate group to act as a good leaving group. Attempts to observe the intermediate en route to **2a** (Scheme 2) by in situ ^{11}B NMR spectroscopy revealed a sharp signal at $\delta = -17.1$ ppm during the first few minutes of the reaction at 25 °C. This chemical shift suggested B–C bond formation concurrent with the quaternization of boron yielding a borate intermediate. While normally the reactions to afford **2** were homogeneous in CH_2Cl_2, **1a** and $B(C_6F_5)_3$ gave single crystals of **3a** immediately after mixing, which were suitable for X-ray diffraction analysis (Figure 2). This structure confirms the proposed reaction

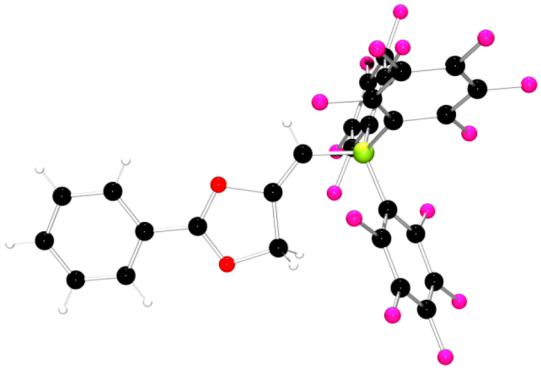


Figure 2. POV-ray depiction of the molecular structure of **3a**. C, black; O, red; F, pink; B, yellow-green.

mechanism. It is interesting to note the similarity between this reactivity and that of Lewis acidic transition metals such as gold or platinum.[20] These transition metals undergo a similar initial 1,2-acyl-oxy shift with terminal alkynes leading to electrophilic metal-carbenoids, although such intermediates have never been isolated.[20] In this respect, the isolation of **3a** represents the first

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crystallographic characterization of an intermediate in such acyl−oxy shift reactions.

Furthermore, we investigated the propargyl rearrangement process utilizing the enantiomerically pure (*S*)-**1c** propargyl ester and observed the formation of the racemic allyl boron compound **2c** by chiral HPLC−MS (see the Supporting Information).[21] Temperature-dependent chiral HPLC measurements indicate no racemization of the allyl boron compound itself up to 60 °C. This loss in chirality transfer is suggesting a nonconcerted mechanism in which ring-opening of **3** proceeds prior to C_6F_5 group migration (Scheme 2).

Interestingly, these allyl boron compounds (**2**) are quite stable in contrast to other compounds incorporating C(sp^3)−B bonds.[2] For example, compound **2a** could be purified by an aqueous workup with 3 M NaOH, even in the presence of hydrogen peroxide, under air and is a bench stable white solid. This stability can be attributed to the steric shielding of the boron center and the intramolecular ester-boron chelate. Subsequent heating of compounds **2a** or **2b** at 45 °C resulted in an irreversible allyl boron migration affording the compounds **4a** and **4b**, respectively (Scheme 3), as evidenced

Scheme 3. 1,3-Allyl Shift Products

R = Ph **4a**, Me **4b**, *p*-tol **4c**

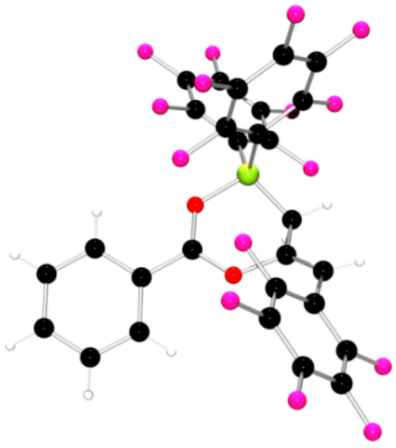
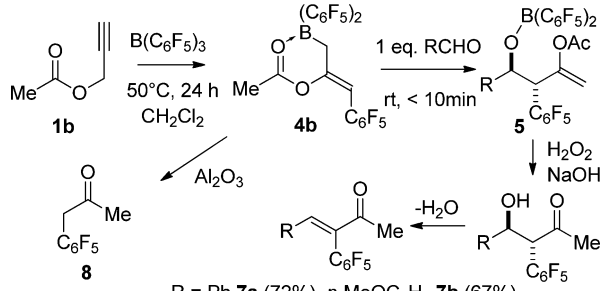


Figure 3. POV-ray depiction of the molecular structure of **4a**. C, black; O, red; F, pink; B, yellow-green. The analogous structure of **4c** is deposited in the Supporting Information.

by spectroscopic data and confirmed by a crystallographic study of **4a** (Figure 3). Compound **4c** could also be synthesized from the reaction of the corresponding propargyl ester with $B(C_6F_5)_3$ and was structurally characterized (see the Supporting Information). While **2a** required prolonged heating to be converted to **4a**, the acetate compound (**2b**) undergoes a clean 1,3-allyl boron shift within 24 h at 45 °C. These 1,3-boron allyl-shifts are reminiscent of the conversion of allyl boranes to the more thermodynamically stable isomers in which the boron atom is located on the least substituted carbon atom.[22]

The applications of these novel allyl boron compounds in organic synthesis were subsequently investigated. In situ generated compound **4b** reacted cleanly, and in <5 min, at room temperature with benzaldehyde to afford the allylation product **5** as a single diastereomer (Scheme 4). While the clean

Scheme 4. Tandem Rearrangement−Addition Process Leading to *α,β*-Unsaturated Ketones



R = Ph **7a** (72%), *p*-MeOC$_6$H$_4$ **7b** (67%), *p*-NO$_2$C$_6$H$_4$ **7c** (58%), Me **7d** (66%), *n*-Pr **7e** (68%), *t*-Bu **7f** (55%)

formation of **5** was consistent with in situ NMR studies (see the Supporting Information), the isolation of **5** proved challenging. Nonetheless, treatment of the reaction mixture under oxidative conditions ($NaOH/H_2O_2$) generated the hydrolyzed sensitive *β*-hydroxy ketone **6a**. This species eliminates water upon column chromatography to generate the *α,β*-unsaturated ketone **7** (see the Supporting Information). The molecular structure of compound **7a** was confirmed by an X-ray diffraction study (Figure 4). In a similar fashion, the *α,β*-

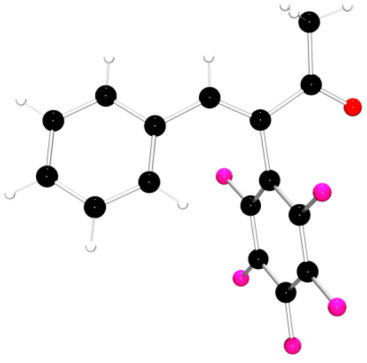


Figure 4. POV-ray depiction of the molecular structure of **7a**. C, black; O, red; F, pink.

unsaturated ketone analogues **7b−f** were also prepared (Scheme 4) from the reactions of **1b** and $B(C_6F_5)_3$ with a variety of aldehydes, thus demonstrating the broad scope of the allylation reactions. The high yielding, multistep reactions to **7** represent a facile route to trisubstituted alkenes with exclusive *E*-configuration. Interestingly, in the absence of aldehyde, species **4b** is converted to the *α*-C_6F_5 substituted ketone **8** when subjected to column chromatography. In this reaction, three processes have taken place including (i) ester hydrolysis, (ii) enol−keto tautomerization, and (iii) protonation of the C−B bond.

The corresponding reaction of **2c** (generated in situ) with aldehydes resulted in the selective and clean formation of the formal *trans*-crotylation products **9** (Scheme 5). After oxidative aqueous workup, the *β*-hydroxy enol esters **10** could be isolated as single diastereomer. This reaction provides a route to the rapid synthesis of *β*-hydroxy enol esters (**10a−10f**) as a single diasteromer (Scheme 5). The relative stereochemistry and the

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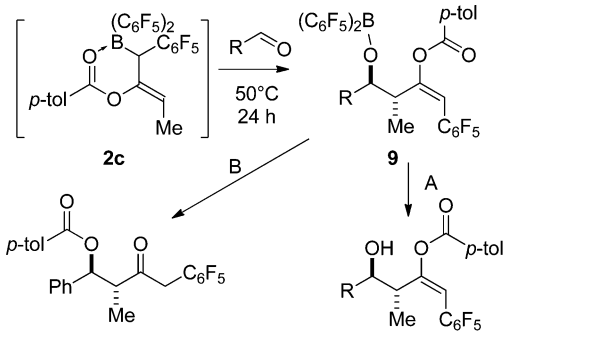
Scheme 5. Diastereoselective Crotylation Reactions[a]



[a]Reactions performed on a 0.50 mmol scale (0.2 M in CH_2Cl_2). (A) H_2O_2/NaOH; SiO_2; (B) H_2O_2/NaOH; neutral aluminum oxide.

enol ester geometry were unambiguously confirmed by an X-ray crystallographic analysis of **10a** (Figure 5). Interestingly,

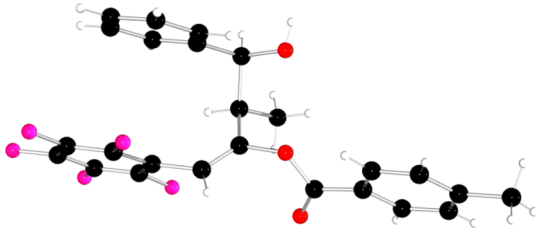
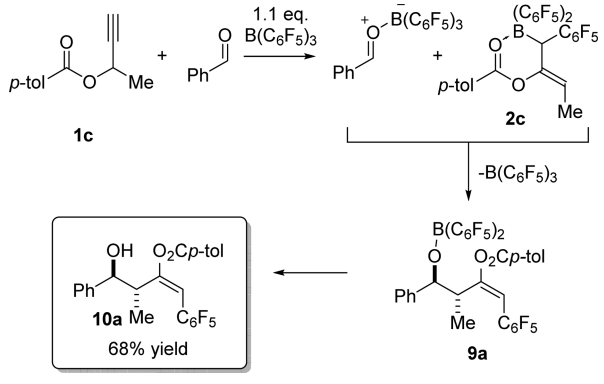


Figure 5. POV-ray depiction of the molecular structure of **10a**. C, black; O, red; F, pink.

purification by column chromatography on silica gel allowed the isolation of the enol esters (**10**), whereas use of neutral aluminum oxide cleanly gave the rearranged product **11**. The formation of **11** arises from an intramolecular 1,3-acyl shift (transesterification) reaction concurrent with an enol−keto tautomerization, presumably triggered by Lewis-acidic sites on the neutral aluminum oxide.

The aforementioned allylation reactions were sequential one-pot processes in which the first step (formation of the allyl boron compound) was monitored before aldehyde addition. The formation of **10a** was also achieved in a one-pot process by mixing all components at the start of the reaction (Scheme 6);

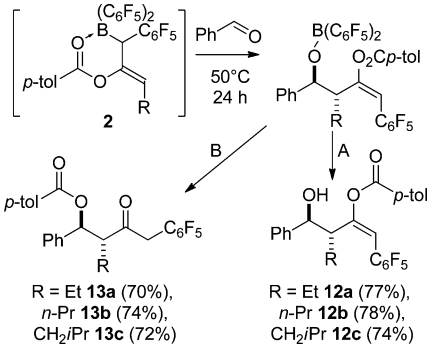
Scheme 6. Dual Role of $B(C_6F_5)_3$ − One-Pot Crotylation Sequence from the Aldehyde/Propargyl Ester Mixture



the combination of aldehyde, propargyl ester, and $B(C_6F_5)_3$ in a 1:1:1.1 ratio with heating to 50 °C generated the expected intermediate (**2c**) as evidenced by NMR spectroscopy. These signals ultimately collapse to the final crotylation product **9**, which afforded **10a** on workup (Scheme 6). $B(C_6F_5)_3$ coordination to the aldehyde significantly diminishes the rate of the boron propargyl-allyl rearrangement as a result of reduced free $B(C_6F_5)_3$ available for alkyne activation (the equilibrium constant for adduct formation between $B(C_6F_5)_3$ and an aldehyde is 10^2 times stronger than that with an ester[19]). However, it is found that $B(C_6F_5)_3$ synergistically accelerates the allylation process because it both enables the irreversible formation of the allyl boron compound **2c** and activates the aldehyde to nucleophilic attack yielding **9** (Scheme 6).[23]

By simply changing the R-group on the propargyl ester, a straightforward route to access various allylation products is possible in a single one-pot transformation. For example, reactions of in situ generated allyl boron compounds **2** with benzaldehyde yield a single diastereomer of the species **12a−c** when purified by column chromatography on silica, while purification on neutral aluminum oxide provides the corresponding rearranged ketones **13a−13c** in good isolated yields (Scheme 7). Spectroscopic data clearly support the formulation of these products, and the structure of **13b** was also confirmed by X-ray diffraction (Figure 6).

Scheme 7. Diastereoselective Allylation by Propargyl-Allyl Rearrangement[a]



[a]Performed on a 0.50 mmol scale (0.2 M in CH_2Cl_2). (A) H_2O_2/NaOH; SiO_2; (B) H_2O_2/NaOH; neutral aluminum oxide.

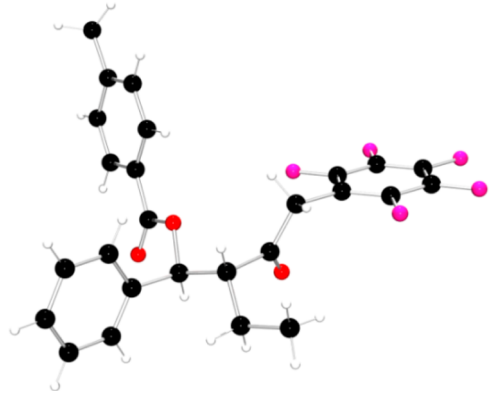


Figure 6. POV-ray depiction of the molecular structure of **13a**. C, black; O, red; F, pink.

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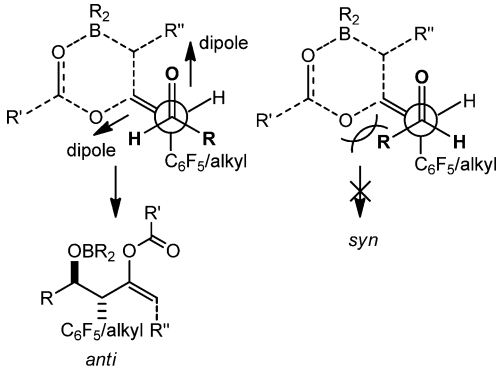
While boron-allylation reactions normally proceed via a closed six-membered Zimmermann–Traxler transition state,[5] in this case, the boron allylation appears to represent a unique example of an open transition state addition as the intramolecular ester chelate presumably inhibits the aldehyde coordination. Nonetheless, open transition state allylation reactions seen with tin or silicon allylation reagents normally result in only poor diastereoselectivities;[5c] the present reactions afford exclusive *anti*-addition stereochemistry. This is a result of the exclusive formation of only one (*Z*)-enol ester diastereomer in the initial boron rearrangement process. It is proposed that the R-group of the aldehyde is placed in an antiperiplanar position to the bulky ester group, maximizing the dipole–dipole interactions of the two C–O bonds, thus fixing the resulting geometry (Scheme 8). While opening of the boron

Scheme 8. Stereochemical Rationale for the *anti*-Allylation Product



ester chelate, followed by aldehyde coordination and allylation via a classical Zimmermann–Traxler transition state, cannot be ruled out, allylations with **2c** proceed rapidly, suggesting that this route is unlikely.

CONCLUSIONS

We have demonstrated the synthesis of a variety of novel allyl boron compounds from the reactions of Lewis acidic $B(C_6F_5)_3$ with propargyl esters. These reactions proceed via a rearrangement process consisting of (i) cyclization via an intramolecular 1,2-addition of the ester to the alkyne activated by $B(C_6F_5)_3$, (ii) ring-opening followed by a C_6F_5-group migration, and (iii) allyl boron migration in the case of no substitution adjacent to the ester oxygen. This sequence of reactions leads to novel allyl–boron compounds and the first formal 1,3-carboboration products. Finally, we have shown that these allyl boron compounds show excellent reactivity as *anti*-selective allylation reagents, introducing a functionalized C3-fragment together with a C_6F_5-group. The resulting β-hydroxy esters are difficult to access via traditional chemistry and are suitable for further functionalization. Indeed, polyfluoroarenes are an important class of molecules in various areas such as pharmaceuticals, agrochemicals, electronic devices, etc.[24] For example, in medicinal chemistry, it has been shown that replacing C_6H_5 with C_6F_5 induce significantly increased biological activity.[25] As both propargyl esters and $B(C_6F_5)_3$ are readily accessible, this chemistry provides a powerful and facile route to a diverse array of allylation products in a one-pot process. The further application of these allyl boron reagents and propargyl ester rearrangements in organic chemistry is the target of continued efforts.

ASSOCIATED CONTENT

Supporting Information

Experimental details for the synthesis of starting materials and new compounds, NMR spectra, and crystallographic information files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

dstephan@chem.utoronto.ca
hashmi@hashmi.de

Author Contributions

[§]These authors contributed equally.

Notes

The authors declare no competing financial interest.

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