ORGANOMETALLICS

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Pathways to Functionalized Heterocycles: Propargyl Rearrangement using $B(C_6F_5)_3$

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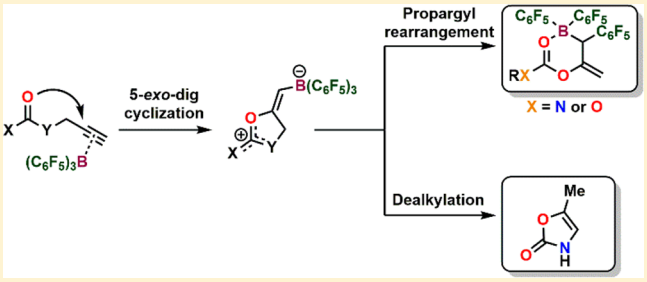
Supporting Information

ABSTRACT: The reactions of propargyl amides, ureas, carbamates, and carbonates with $B(C_6F_5)_3$ proceed via an intramolecular 5-*exo-dig* cyclization across the alkyne unit to yield the corresponding vinyl borate species. The generated sp^2 carbocation is stabilized by the flanking heteroatoms, allowing for isolation of oxazoline intermediates. The fate of these intermediates is strongly dependent upon the propargyl-functionalized starting material, with the carbamates and carbonates undergoing a ring-opening mechanism (propargyl rearrangement) to give cyclic allylboron compounds, while prolonged heating of the urea derivatives shows evidence of oxazole formation. In a deviation away from the reactivity of carbamates stated previously, the benzyl carbamate substrate undergoes dealkylation at the benzylic position, liberating 5-methyloxazol-2-(3*H*)-one.



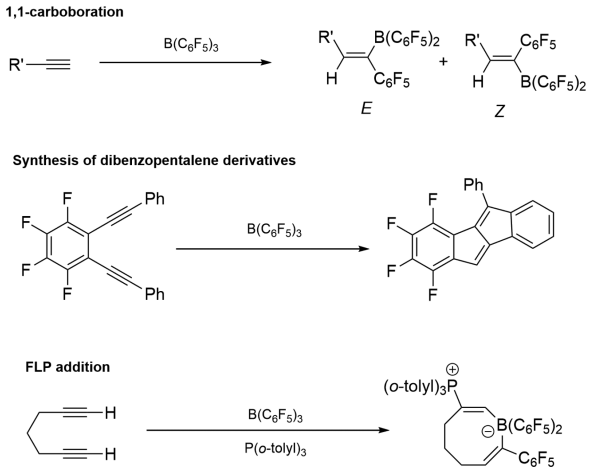
INTRODUCTION

Functionalized heterocycles are key components of a diverse range of both natural products and synthetic pharmaceuticals. Oxazoles are particularly important for their role in a range of biologically active compounds, including anti-inflammatory,[1] antirheumatic,[2] and antidiabetic[3] treatments inter alia.[4] In addition to these applications, oxazoles and oxazolines have been used as ligands in coordination chemistry[5] and as protecting groups.[6]

Given their prominent position in a range of pharmaceutical products, investigations into alternative pathways utilizing main-group elements are becoming more attractive, as the formation of such heterocyclic structures through cyclization reactions are most often effected via transition-metal catalysts such as gold,[7] palladium,[8] and silver.[9] Nevertheless, recent developments have led to alternative approaches in which the d-block metal is replaced by a main-group element.[10] More recently Saito et al. reported an elegant methodology involving an iodine-mediated oxidative annulation reaction between an alkyne and nitrile that proceeds via the formation of an alkenyliodonium intermediate followed by reductive elimination to give the 2,4,5-trisubstituted oxazole.[11]

Research by Erker et al. has shown a strong propensity for 1,1-carboboration when tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, is reacted with terminal alkynes.[12] While gold and other π Lewis acidic transition metals can form strong interactions with π bonds,[13] an analogous boron π bond complex has yet to be isolated, although weak van der Waals interactions have been detected.[14] Further to this, a range of cyclization reactions have been shown to occur when terminal and internal diyne substrates have been used, giving a broad product range including fused polycyclic dibenzopentalene units[15] as well as five-membered boracyclic compounds (Scheme 1).[16] When diynes are used in conjunction with

Scheme 1. Previous Work on $B(C_6F_5)_3$-Promoted Rearrangement Reactions



Received: September 3, 2015

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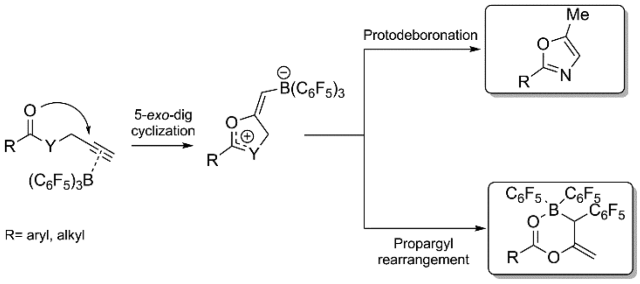
DOI: 10.1021/acs.organomet.5b00753
Organometallics XXXX, XXX, XXX−XXX

bulky phosphine reagents such as P(*o*-tolyl)$_3$ as the Lewis basic component of a frustrated Lewis pair (FLP) system, 1,1-carboboration occurs with subsequent 1,2-addition of the second alkyne unit, resulting in an eight-membered heterocyclic product (Scheme 1).[12b,17] In addition to this, contemporary work has indicated that $B(C_6F_5)_3$ is an extremely versatile reagent for oxazole formation from amide precursors.[18] The reactivity of $B(C_6F_5)_3$ has also been exploited for use as an allylation reagent generated by propargyl ester rearrangement.[19]

However, the increasing interest in main-group-mediated chemistry has led to a new focus on the application of p-block elements over precious transition metals. Our previous research on the activation of terminal alkynes using the strong Lewis acid $B(C_6F_5)_3$ showed that propargyl amides underwent an intramolecular cyclization reaction to form oxazolines and oxazoles,[18] while propargyl esters rearranged to give allylboron reagents or dioxolium compounds (Scheme 2).[19,20] These studies have led us to explore further the range of functional groups which are amenable to these main-group activation reactions to generate heterocyclic compounds.

Scheme 2. Previously Observed Reactivity of Terminal Propargyl Amides and Esters with $B(C_6F_5)_3$



While previous work focused solely on propargyl esters or amides (Scheme 2), the current work describes the applications of $B(C_6F_5)_3$ to these types of propargyl rearrangements and gives a detailed view into the influence of the functionality installed in the propargylic position (see Figure 1).

■ RESULTS AND DISCUSSION

Reactivity of Dipropargyl Amides. In investigations of dipropargyl amide systems, it was questionable whether a diyne cyclization reaction similar to those reported by the Erker group would proceed (Scheme 1),[15a] or if the propargyl amide cyclization would be the favored reaction pathway.[21] In the latter case the additional alkyne functionality would enable further reactions or tandem processes. Interestingly, when *N,N*-dipropargyl amides **1** and $B(C_6F_5)_3$ were reacted in a 1:1 ratio, exclusive formation of the 5-*exo*-oxoboration cyclization product **8** (Scheme 3) was observed, with the second alkyne unit remaining untouched. This reactivity follows a pathway analogous to that previously observed where the N-substituted propargyl amides undergo a 1,2-addition process to give a vinyl borate species.[18]

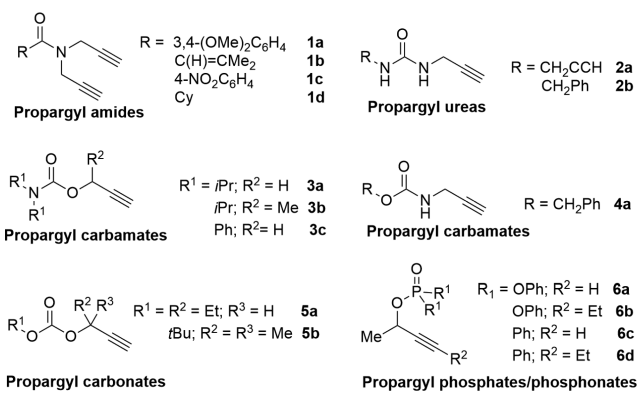
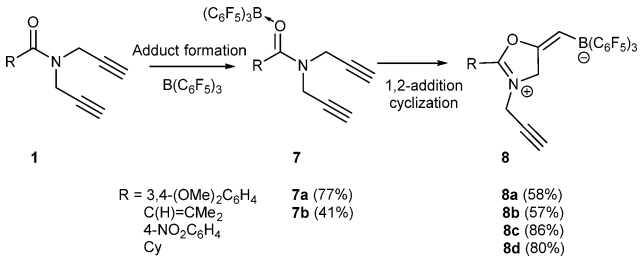


Figure 1. Propargyl-functionalized starting materials discussed herein.

Scheme 3. Reactions of Dipropargyl Amide Derivatives with $B(C_6F_5)_3$



The initial species formed upon mixing *N,N*-dipropargyl amides **1** and $B(C_6F_5)_3$ was the Lewis acid/base adduct between the Lewis basic amide oxygen atom and the vacant p orbital on boron. The resultant compounds **7a,b** were isolated in 77% and 41% yields, respectively, and structurally characterized (vide infra). Subsequent cyclization via π activation of one of the terminal alkynes was achieved by heating to 45 °C for 2 days to give compounds **8**. The time frame was reduced to 60 min at room temperature, giving very good conversion (86%) for the electron-withdrawing *p*-nitro-substituted aryl group (**8c**). This would suggest that the electron-withdrawing effect of the nitro group reduces the Lewis basicity of the amide oxygen, therefore increasing the dissociation of the adduct. This in turn leads to greater concentrations of unbound $B(C_6F_5)_3$ in solution, which is able to activate the π system of the alkyne toward cyclization. This trend holds true for other experimental results seen in this investigation and is in accordance with our recent studies in this area.[18]

The formation of adducts **7** can be used to elucidate the reaction pathway whereby the initial B−O Lewis adduct is formed in equilibrium with the dissociated $B(C_6F_5)_3$. The free Lewis acid then activates the π system of the alkyne toward cyclization, as evidenced by the presence of two peaks in the ^{11}B NMR spectra, one at ca. δ −0.5 ppm for the dative B−O adduct and a second at ca. δ −16.9 ppm associated with the rapid ensuing cyclization. The expected 5-alkylidene-4,5-dihydrooxazolium borate products (**8**) were characterized by multinuclear NMR spectroscopy, all of which displayed sharp singlets in the ^{11}B spectra between δ −16.9 and −17.0 ppm, indicating the formation of the aforementioned four-coordinate vinyl borate species. This is supported by the ^{19}F NMR spectra, which showed three signals in a 2:2:1 ratio as a result of the ortho (δ −132.7 to −132.8 ppm), meta (δ −164.7 to −165.3 ppm), and para (δ −160.3 to −160.9 ppm) fluorine atoms of the pentafluorophenyl rings. In accordance with previous work the π activation of the alkyne and cyclization gives the 1,2-addition product in the *E* configuration exclusively.[18]

Single-crystal X-ray diffraction was used to explore the solid-state structures of the majority of the compounds produced in

DOI: 10.1021/acs.organomet.5b00753
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these reactions. The initial B−O adducts **7** between $B(C_6F_5)_3$ and the carbonyl oxygen of the dipropargyl amide crystallized readily from solution, and their solid-state molecular structures are shown in Figure 2. The metrics for adducts **7a,b** are very

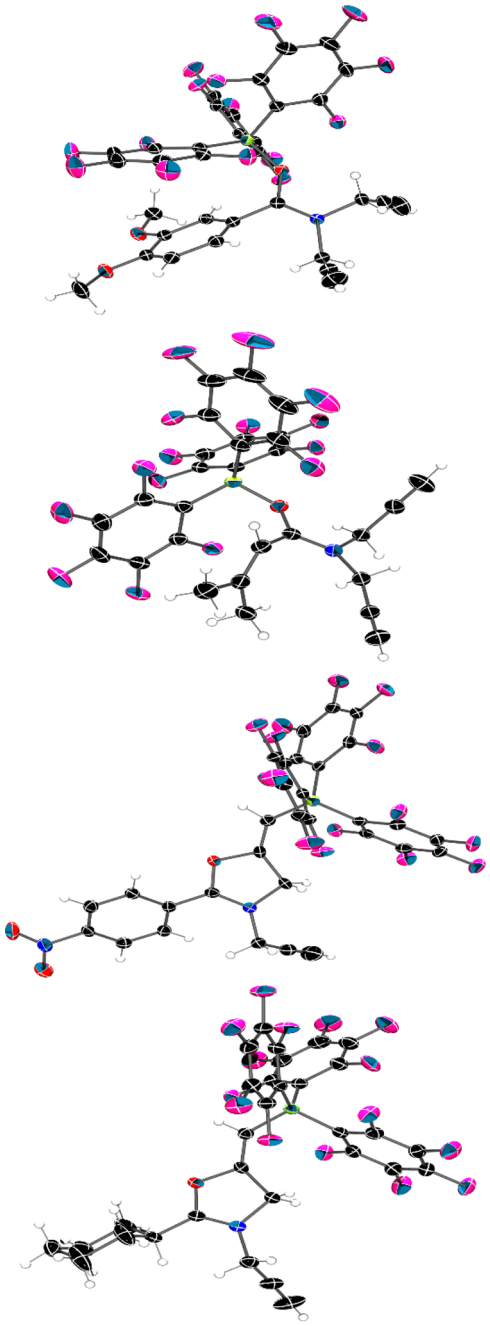
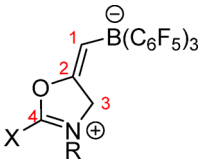


Figure 2. Solid-state structures of **7a,b** and **8c,d** (from top to bottom). Toluene solvent is omitted for clarity. Color code: B, yellow-green; C, black; N, blue; F, pink; O, red. Thermal ellipsoids are shown at 50% probablility.

similar to individual bond lengths within the expected range, albeit with a very slight contraction of the C^4−N bond (ca. 1.324 Å), reflecting stabilization of the cationic carbonyl oxygen via resonance. In both cases the donation of the lone pair of the sp^2 orbital on oxygen leads to a bent geometry and a cis configuration with respect to the substituent R group. The molecular structures of **8c,d** (Figure 2, Table 1) show the

Table 1. Experimental Bond Lengths for 8c,d and 9a,b



bond	bond length/Å			
	8c	8d	9a	9b
C^1−C^2	1.303(4)	1.315(2)	1.309(3)	1.310(4)
C^2−C^3	1.503(4)	1.510(2)	1.512(3)	1.508(5)
C^3−N	1.475(4)	1.475(2)	1.465(2)	1.455(4)
C^4−N	1.300(3)	1.298(2)	1.313(3)	1.312(5)
C^4−X	1.468(4)	1.489(2)	1.317(2)	1.309(5)
C^2−O	1.468(3)	1.459(2)	1.461(2)	1.460(4)
C^4−O	1.305(4)	1.307(2)	1.304(2)	1.309(4)
C^1−B	1.623(4)	1.628(2)	1.619(3)	1.618(5)

product of the intramolecular cyclization reaction of the dipropargyl amides **1c,d** with $B(C_6F_5)_3$. Delocalization of the positive charge about the N−C^4−O moiety is indicated by a shortening of both the C^4−O bond (ca. 1.305 Å) and the C^4−N bond (ca. 1.299 Å) in comparison to those of a formal single bond at 1.368 and 1.346 Å, respectively.[22] Another point of note is the rotation of the *p*-nitrophenyl group of **8c** out of the O−C^4−N plane by ca. 41°. This observation may be reasoned simply as the result of reduced steric strain between the adjacent propargyl group and the C^4 substituent in these orientations. The structural parameters are presented in the Supporting Information.

The reactivity observed here clearly shows that the propargyl amide cyclization is outcompeting any potential diyne cyclization or 1,1-carboboration mechanisms. Furthermore, the second alkyne moiety remains untouched and enables the potential for further functionalization such as hydroboration or application in tandem processes.

Reactivity of Propargyl Ureas. In an effort to gain an insight into the reactivity of the Lewis basic carbonyl of these 5-*exo-dig* cyclization reactions, the amide carbon substituent was replaced with a strongly donating secondary amine to give the corresponding urea derivative (**2**) that was anticipated to give the 5-alkylidene-4,5-dihydrooxazol-2-amino borate species (**9**). Observation of the ^{11}B NMR spectra of the reaction between compounds **2a,b** and $B(C_6F_5)_3$ showed little to no conversion to the corresponding 5-alkylidene-4,5-dihydrooxazol-2-amino borate product (**9**; Scheme 4) after 2 days at ambient temperature. However, broad resonances in the δ −1.6 to −1.8 ppm region of the ^{11}B NMR spectra did indicate adduct formation.[23] Upon heating at 50 °C for 7 days (**9a**) or 14 days (**9b**), a sharp peak emerged at ca. δ −17.0 ppm representing the expected four-coordinate vinyl borate species which were both generated in yields of 31%. Prolonged heating of the reaction mixture with **2b** led to a further rearrangement, as indicated by a new broad peak at δ −10 ppm (Figure 3), which is attributed to the oxazole compound **II** (Figure 3).

The reduced reaction rates for these transformations can be attributed to two main components, the first being the sparse solubility of the urea substrates in a range of organic solvents which leads to increased reaction times. The second relates to the stronger donor ability of the urea in comparison to the amide functionality as well as the stabilizing effect of the delocalized positive charge about the N_2CO fragment, giving

DOI: 10.1021/acs.organomet.5b00753
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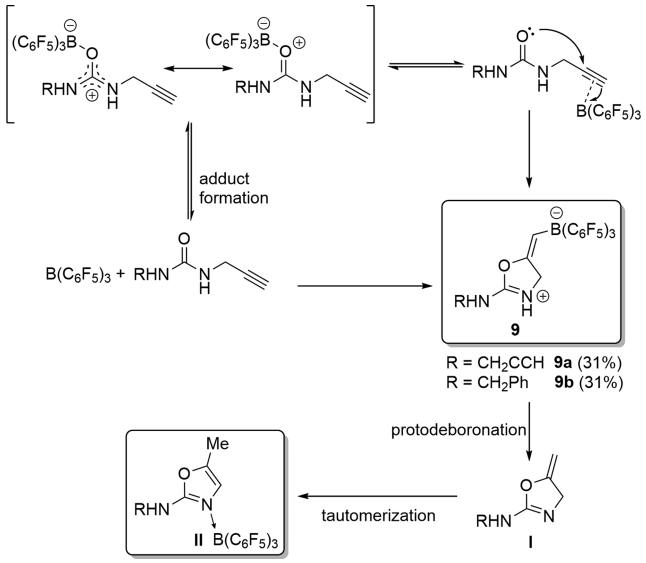
Scheme 4. Proposed Mechanistic Pathway of the Reaction between Propargyl Ureas and $B(C_6F_5)_3$



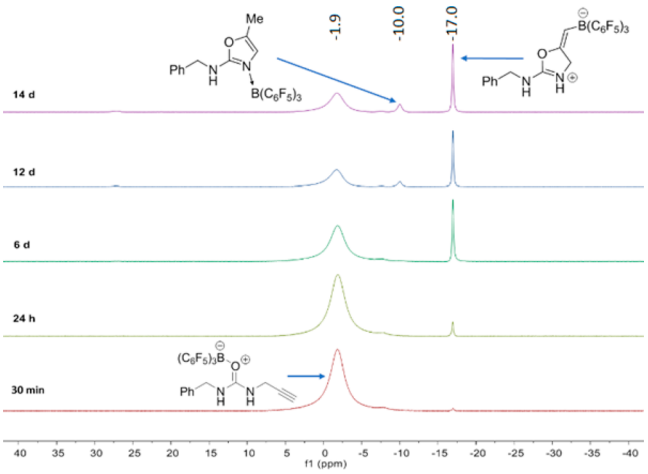


Figure 3. In situ ^{11}B NMR spectra of the reaction between **2b** and $B(C_6F_5)_3$.

stronger adduct formation. This stabilized adduct would lower the concentration of dissociated free $B(C_6F_5)_3$, leading to reduced rates of π activation of the alkyne. Therefore, more harsh reaction conditions are required to ensure conversion of **2** to the corresponding 2-amino-5-alkylidene-4,5-dihydrooxazole borate species (**9**) and subsequent protonation/tautomerization to the 2-amino-5-methyl-4,5-dihydrooxazole product **II** (Scheme 4). Workup of the reaction mixtures from **2a,b** after the appropriate time gave colorless crystals of **9a,b** (Figure 4).

The ^{11}B NMR spectra confirmed the assignments made from the in situ studies that are supported by the ^{19}F NMR spectra, which reveal three resonances in a 2:2:1 ratio for the ortho (δ −132.1 to −132.6 ppm), meta (δ −165.1 to −165.2 ppm), and para (δ −161.1 to −161.3 ppm) aryl fluorine atoms closely akin to those seen previously with the products from the analogous reactions with dipropargyl amides.

Earlier assumptions that the cationic charge generated by the cyclization step could be delocalized about the structure via lone pair donation from the adjacent heteroatoms into the vacant p orbital of the carbocation were further validated on

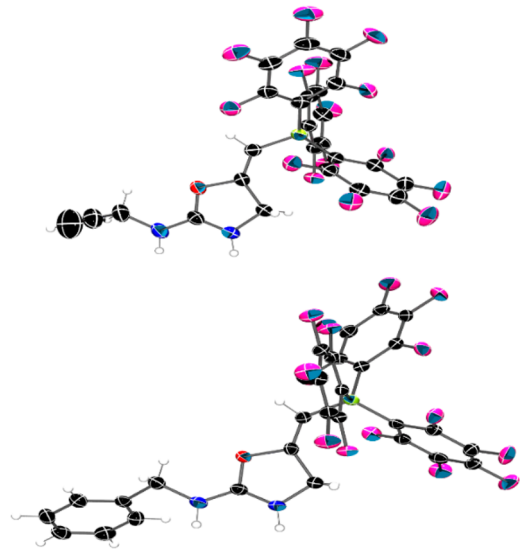
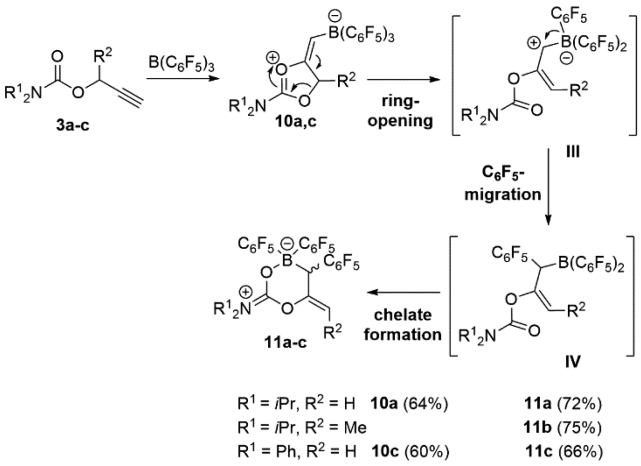


Figure 4. Solid-state molecular structures of **9a** (top) and **9b** (bottom). Color code: B, yellow-green; C, black; N, blue; F, pink; O, red. Thermal ellipsoids are shown at 50% probability.

analysis of the metric parameters of the structures of **9a,b** (Table 1). Both data sets agree well with expected bond lengths, with both the C^4–N^1 and C^4–N^2 bonds being between the accepted values for single and double C–N bonds at ∼1.313 Å. This is clarified further on investigation of the planarity of the N_2CO fragment, with the N^2–C^4–N^1–C^3 fragment of **9a** showing a torsional angle of −179.8(2)°.

Reactivity of Propargyl Carbamates. In contrast to the reactivity of ureas, the carbamates underwent a more complicated cyclization/ring-opening mechanism (propargyl rearrangement) upon addition of $B(C_6F_5)_3$ to **3a−c**. Although the cyclization to intermediates **10a,c** proceeded under mild conditions to give yields of 64% and 60% respectively, long reaction times (24−120 h) were needed to afford the final allylboron products **11a−c** (Scheme 5). Complete reaction of **3a** to give **11a** with $B(C_6F_5)_3$ was achieved in 16 h when the temperature was raised to 50 °C. These carbamates behave in a manner similar to that for the propargyl esters upon treatment with $B(C_6F_5)_3$.[19] In order to probe further the mechanism for the generation of the allylboron compounds **11**, which contain a carbamate-boron chelate, the reactions were performed at low

Scheme 5. Reaction between 3 and $B(C_6F_5)_3$ To Give 11



DOI: 10.1021/acs.organomet.5b00753
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temperature (retarding the ring-opening step) to enable isolation of the 2-amino-1,3-dihydrooxolium intermediates (**10**). Previously reported rearrangements of dihydrooxolium compounds were rapid, with unstabilized propargyl esters giving the resultant allylboron reagent in as little as 15 min with the quaternary boron intermediate proving very challenging to isolate.[19] However, the inclusion of the amido nitrogen appears to aid the stabilization of the delocalized cationic charge about the NCO_2 moiety in **10**, leading to isolation of the corresponding intermediates. Analysis of intermediates **10a,c** was carried out by multinuclear NMR spectroscopy using cooled deuterated solvent to delay further reactions. The NMR spectra exhibited typical characteristics of such vinyl boron complexes, with a single sharp resonance being seen in the ^{11}B NMR spectra (δ −17.0 ppm) and three peaks in the ^{19}F NMR spectra in a 2:2:1 ratio for the ortho (δ −133.0 to −132.6 ppm), meta (δ −166.2 to164.9 ppm), and para (δ −161.9 to −160.5 ppm) fluorine atoms of the perfluorophenyl rings. When the reaction mixture was warmed to room temperature, the ensuing rearrangement reaction proceeded, yielding the allylboron species **11** (Scheme 5).

These allylboron compounds **11** could be identified by a typically broad peak at ca. δ 0.0 ppm in the ^{11}B NMR spectra signifying the new B−O adduct. More prominent features of these products are the vinylic proton resonances seen in the ^{1}H NMR spectra, which occur as doublets (**11a,c**) or a quartet (**11b**) in the δ 4.3−5.0 ppm region. The conversion of **10** to **11** leads to a change in the ^{19}F NMR spectra, with the three originally identical C_6F_5 rings giving way to nine new peaks of the now inequivalent perfluorophenyl rings of **11**.

There is an emerging trend whereby an increase in the number of stabilizing heteroatoms flanking the carbocation decreases the ease of the 5-*exo*-oxoboration cyclization. There is basis for the argument that increasing the Lewis basicity of the carbonyl oxygen would cause the reaction to undergo a more rapid cyclization once dissociation occurs.[20] However, the rate-determining step of the reaction is the cleavage of the B−O dative bond; hence, if this bond is stabilized via resonance of the N_2CO moiety, then the rate of conversion is stunted.

Importantly, the additional amido group not only stabilizes the intermediate **10** but also increases the stability of the boron chelate in **11**. Prolonged heating of **11a** at 60 °C did not lead to the 1,3-carboboration product through a 1,3-allylboron shift, showing reactivity different from that of the propargyl esters.[19] In addition to the in situ multinuclear NMR analysis of the propargyl carbamate rearrangement, the intermediates **10** and the allylboron compounds **11** (Figure 5) were structurally characterized by single-crystal X-ray diffraction. The solid-state structures of **11b,c** verify the outlined trans-oxyboration mechanism presented in Scheme 5. The structural parameters are summarized in Tables 2 and 3.

Upon comparison of the structures of these intermediates (**10**) with those formed with the propargyl ureas (**9**), it is noted that the C−N bond distance in **9a** is longer than that of **10a** at 1.313(3) vs 1.290(3) Å, respectively. This is in good agreement with the more strongly electron donating effect of the single amino group in comparison with the stabilization over the two amino functionalities in the urea derivatives.

Examination of the solid-state structures of the products **11b,c** (Figure 5 and Table 3) confirmed the rearrangement of the vinyl borate compounds **10b,c** to give the corresponding six-membered allylboron heterocycles. Inspection of the metric parameters show the expected bond lengths for the predicted

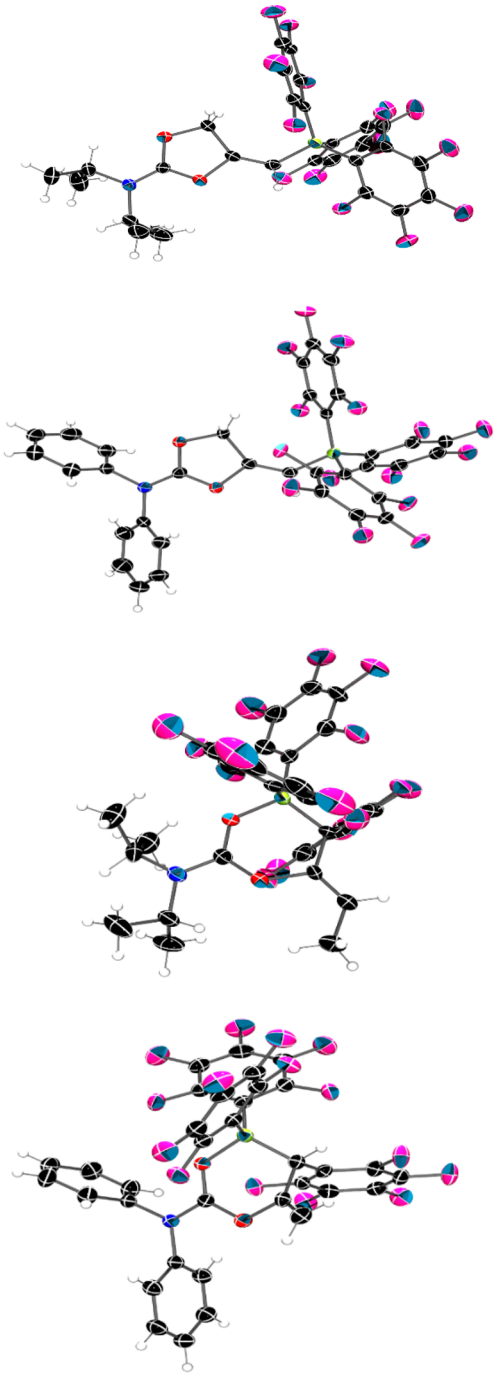

Figure 5. Solid-state molecular structures of **10a,c** and **11b,c** (from top to bottom), Color code: B, yellow-green; C, black; N, blue; F, pink; O, red. Thermal ellipsoids are shown at 50% probability.

structure, with the C^2−C^3 bond exhibiting typical double-bond character (1.309(3) Å) and shortening of the C^4−N bond (1.320(3) Å) in accordance with previous assertions regarding the bond order (Table 3).

The former transformations used propargyl carbamates which were derived from propargyl alcohols. The reverse combination of a propargyl carbamate derived from a propargyl amine was also investigated in the reaction with $B(C_6F_5)_3$ (Scheme 6). On investigation of the reaction between compound **4** and $B(C_6F_5)_3$ an unexpected result was observed whereby the anticipated stable zwitterionic species was not the major product of the reaction. Multinuclear NMR spectro-

DOI: 10.1021/acs.organomet.5b00753
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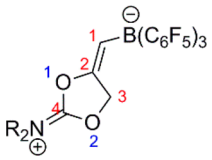
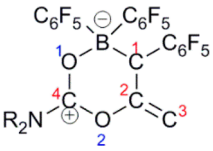
Table 2. Experimental Bond Lengths for 10a,c



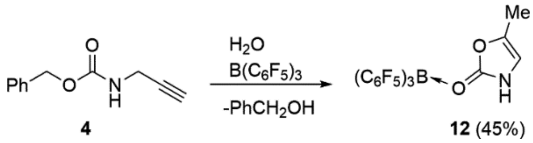
bond	bond length/Å	
	10a	10c
C^1-C^2	1.302(3)	1.304(4)
C^2-C^3	1.509(3)	1.505(4)
C^3-O^2	1.468(3)	1.466(4)
C^4-O^2	1.309(3)	1.297(3)
C^4-N	1.290(3)	1.305(3)
C^2-O^1	1.440(3)	1.464(3)
C^4-O^1	1.307(3)	1.305(3)
C^1-B	1.616(4)	1.627(4)

Table 3. Experimental Bond Lengths for 11b,c



bond	bond length/Å	
	11b	11c
C^1-C^2	1.498(6)	1.492(3)
C^2-C^3	1.324(7)	1.309(3)
C^2-O^2	1.438(5)	1.436(2)
C^4-O^1	1.280(6)	1.263(3)
C^4-O^2	1.332(6)	1.315(3)
C^4-N	1.325(6)	1.320(3)
C^1-B	1.633(7)	1.647(4)
O^1-B	1.570(6)	1.555(2)

Scheme 6. Oxazolone Synthesis from the Reaction between $B(C_6F_5)_3$ and 4



scopic and X-ray crystallographic (see later) analysis clearly shows the product to be 5-methyl-2-(3*H*)-oxazolone (**12**; Scheme 6) and not the cyclized vinyl borate as observed with similar substrates.

The ^{11}B NMR spectrum of **12** shows a resonance at δ 0.7 ppm indicative of a carbonyl boron adduct, and the ^1H NMR spectrum unmistakably shows the formation of the methyl group produced through isomerization (δ 2.18 ppm) along with the vinyl proton at δ 6.56 ppm. It is presumed that trace amounts of water trigger the dealkylation of the benzyl group after cyclization followed by tautomerization to yield the oxazolone derivative **12**. Attempts to render this transformation catalytic have met with limited success. However, reactions using 10 mol % of $B(C_6F_5)_3$ with 1 equiv of water under ambient conditions show the emergence of a singlet at δ 4.63 ppm in the ^1H NMR, indicating the formation of benzyl alcohol from the dealkylation step. This exemplifies the potential of $B(C_6F_5)_3$ to be used in the formation of such oxazolone derivatives are more often observed in gold or palladium catalysis.[24]

X-ray crystallographic studies of **12** revealed the structure for the 5-methyl-2-(3*H*)-oxazolone-$B(C_6F_5)_3$ adduct (Figure 6).

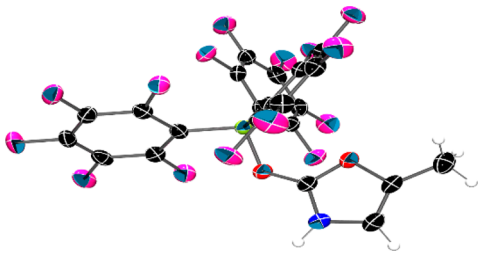
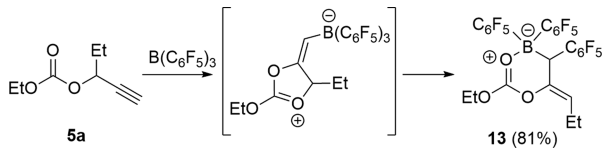


Figure 6. Solid-state molecular structure of **12**, Color code: B, yellow-green; C, black; N, blue; F, pink; O, red. Thermal ellipsoids are shown at 50% probability.

Delocalization of electron density about the carbamate functionality leads to contraction of the heteroatom−carbon bonds as noted above. The structural parameters are summarized in the Supporting Information.

Reactivity of Propargyl Carbonates. To extend the substrate scope, the reactivity of propargyl carbonates was investigated. It was seen that the reaction of **5a** with $B(C_6F_5)_3$ proceeded in the same fashion as for the propargyl esters and carbamates, displaying comparable stability of the intermediate, leading to a long reaction time of 3 days to give the allylboron product **13**; however, a good yield of 81% was obtained (Scheme 7). Analysis via X-ray crystallography further

Scheme 7. Reactions of Propargyl Carbonate 5a in Propargyl Rearrangements with $B(C_6F_5)_3$



expounded the delocalization about the heteroatom-flanked carbon center, with all three C−O bonds displaying similar lengths of 1.246(2), 1.298(2), and 1.292(2) Å (Figure 7).

In a departure from the observed reactivity of these systems described above, the introduction of a *tert*-butyl group to the

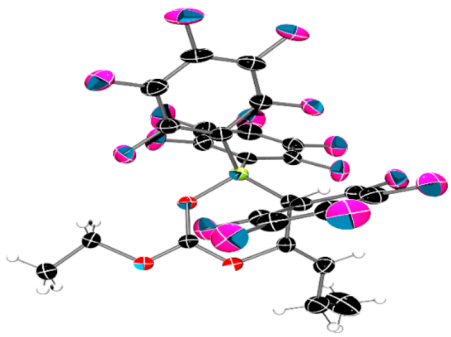


Figure 7. Solid-state molecular structure of **13**, Color code: B, yellow-green; C, black; F, pink; O, red. Thermal ellipsoids are shown at 50% probability.

DOI: 10.1021/acs.organomet.5b00753
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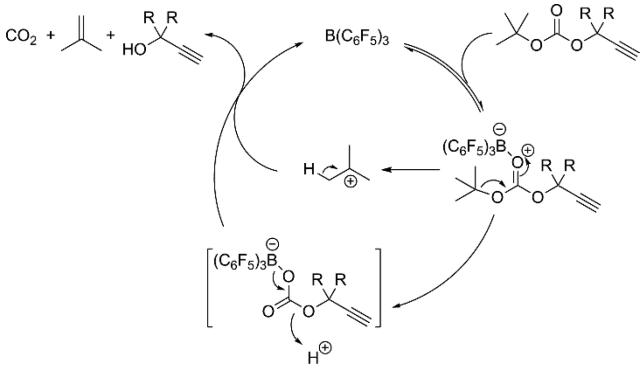
propargyl carbonate as in **5b** resulted in the loss of the Boc group in the presence of $B(C_6F_5)_3$ (Scheme 8).

Scheme 8. Boc Deprotection of Propargyl Carbonates using 10 mol % $B(C_6F_5)_3$



Analysis of the ^{1}H NMR spectra showed that isobutylene was generated in addition to the corresponding propargyl alcohol and CO_2. This was conducted on a catalytic scale using 10 mol % of $B(C_6F_5)_3$, with the ^{1}H NMR spectrum showing almost complete deprotection after 17 h at room temperature, as evidenced by the presence of a septet at δ 4.64 ppm for the isobutylene.

A shift in the resonance position of the methyl groups of the alcoholic moiety from δ 1.70 to 1.67 ppm is also noted. While catalytic deprotection traditionally occurs through the addition of a strong Brønsted acid such as trifluoroacetic acid and HCl/acetic acid, if other acid-sensitive functionalities are present in a given compound, then a milder approach may be necessary.[25] While this conversion has also been effected by other main-group compounds,[26] this is a nice example where tris(pentafluorophenyl)borane has been used for the catalytic removal of Boc protecting groups.

Reactivity of Propargyl Phosphates and Phosphinates. Further substrates were also tested in an attempt to introduce varying heteroatoms into the cyclized product. To this end terminal and internal propargyl phosphates (**6a**,**b**) and phosphinates (**6c**,**d**) were tested in the reaction with $B(C_6F_5)_3$. In the case of **6a** strong adduct formation could be observed and decomposition occurred at elevated temperatures (20 h, 80 °C in C_6D_6), while **6b** decomposed directly upon addition of $B(C_6F_5)_3$. The reactions of propargyl phosphinates **6c**,**d** gave classical adducts which did not undergo further reaction even at elevated temperatures (18 h at 80 °C). These experiments clearly indicate that phosphates and phosphinates behave differently from the previously studied propargyl ester, carbamate, and carbonate systems. This might be attributed to the longer P−O bond and the stronger bond energy of the P−O→B dative bond.

■ CONCLUSIONS

The addition of the strong Lewis acid $B(C_6F_5)_3$ to propargyl amides and ureas provides a potentially catalytic synthetic route to oxazoline derivatives. In contrast to recent studies by the Erker group, this work shows that 5-*exo*-oxoboration of these nonaromatic nitrogen derived diyne systems occurs preferentially over any carboboration steps.[12b] It was seen that π activation of the carbamates and carbonates yields allylboron products via a C_6F_5 migration rearrangement. These species might be useful in aldehyde allylation reactions, and work on this topic and other aspects of the reactivity of these compounds and their applications in organic chemistry is ongoing.

■ EXPERIMENTAL SECTION

General Experimental Considerations. With the exception of the starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. An argon- or nitrogen-filled glovebox (MBraun) was used to manipulate solids, including the storage of starting materials, room-temperature reactions, product recovery, and sample preparation for analysis. All solvents (toluene, CH_2Cl_2, pentane, hexane) were dried by employing a Grubbs-type column system (Innovative Technology) or an MB SPS-800 solvent purification system and stored under a nitrogen atmosphere. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on Bruker Avance III-300, Bruker Avance DRX-300, Bruker Avance II 400, Bruker Avance 500, Bruker Avance III 600, and JEOL Eclipse 300 spectrometers. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS), and ^{1}H/^{13}C signals are referenced to $CDCl_3$ (7.26/77.16 ppm) and CD_2Cl_2 (5.32/53.80 ppm) as internal standards. ^{19}F, ^{31}P, and ^{11}B NMR spectra were referenced to $CFCl_3$ (^{19}F), H_3PO_4 (^{31}P), and $BF_3{\cdot}Et_2O/CDCl_3$ (^{11}B). The description of signals include s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, and br = broad. All coupling constants are absolute values and are expressed in hertz (Hz). Yields are given as isolated yields. All spectra were analyzed assuming a first-order approximation. IR spectra were measured on an FT-IR Bruker Vector 22 machine or Shimadzu IRAffinity-1 photospectrometer. Mass spectra were measured on JEOL JMS-700, Waters LCT Premier/XE, Waters GCT Premier, and Bruker ApexQe hybrid 9.4 spectrometers. Elemental analyses were conducted at London Metropolitan University by Mr. Stephen Boyer or using the in-house services at Heidelberg University.

Synthesis of 1. *General Procedure.* *N*,*N*-Dipropargylcarboxamides were prepared according to literature methods.[21] Et_3N (2.0 equiv) and DMAP (0.02 equiv) were added to a solution of *N*,*N*-dipropargylamine hydrochloride (1.0 equiv) in CH_2Cl_2 at room temperature under a nitrogen atmosphere, and the resulting solution was stirred for 15 min. The solution was then cooled to 0 °C, and the corresponding acyl chloride (1.0 equiv) was added dropwise and stirred for 30 min at this temperature. The reaction mixture was then warmed to room temperature and was stirred for a further 3 h. The reaction was then quenched with water, the aqueous layer was extracted with CH_2Cl_2 (×2), and the combined organic phases were washed with brine. The organic phase was then dried with Na_2SO_4 and filtered. Removal of the solvent yielded the crude product, which was purified by column chromatography.

*Characterization Data for **1a**.* ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 7.22 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.9 Hz, 1H), 7.17 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 6.89 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 4.33 (br s, 4H), 3.91 (s, 3H), 3.91 (s, 3H), 2.33 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): 170.8 (s), 151.0 (s), 148.8 (s), 126.7 (s), 120.8 (s), 111.0 (s), 110.6 (s), 78.6 (br s), 72.8 (br s), 56.1 (s).

*Characterization Data for **1b**.* ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 5.82 (m, 1H), 4.33 (s, 2H), 4.21 (s, 2H), 2.28 (s, 1H), 2.21 (s, 1H), 1.93 (d, $^4J_{HH}$ = 1.1, 3H), 1.86 (d, $^4J_{HH}$ = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): 167.6 (s), 149.6 (s), 116.8 (s), 78.6 (s), 78.1 (s), 73.0 (s), 72.1 (s), 36.8 (br s), 33.3 (br s), 26.6 (br s), 20.5 (br s).

*Characterization Data for **1c**.* ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 8.31 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.74 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 4.50 (br s, 2H), 4.10 (br s, 2H), 2.40 (br s, 1H), 2.32 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): 168.7 (s), 150.0 (s), 140.7 (s), 128.4 (s), 124.1 (s), 77.4 (s), 74.2 (s), 73.2 (s), 38.3 (s), 34.0 (s).

DOI: 10.1021/acs.organomet.5b00753
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*Characterization Data for **1d**.* ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 4.31 (d, $^4J_{HH}$ = 2.1 Hz, 2H), 4.23 (d, $^4J_{HH}$ = 2.1 Hz, 2H), 2.50 (m, 1H), 2.30 (br s), 2.20 (br s), 1.84−1.72 (m, 4H), 1.86 (m, 1H), 1.48 (m, 2H), 1.34−1.16 (m, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): 175.6 (s), 78.8 (s), 78.3 (s), 72.9 (s), 72.2 (s), 41.0 (s), 36.1 (s), 33.9 (s), 29.4 (s), 25.8 (s). HRMS (EI$^+$): *m/z* calculated for [M]$^+$ $C_{13}H_{17}NO^+$ 203.1306, found 203.1310. IR (cm^{-1}): ν_{max} 3281, 3223, 2926, 2922, 2855, 1728, 1643, 1452, 1435, 1418, 1343, 1310, 1290, 1273, 1265, 1244, 1204, 1175, 1136, 953, 922, 893, 856, 640.

Synthesis of 2. *General Procedure.* Propargyl ureas were prepared according to similar literature methods.[27] To the amine (1.00 equiv) dissolved in water (ca. 50 mL) at 4 °C was added carbonyldiimidazole (CDI) (2.00 equiv), and the resulting mixture was stirred for 1 h at this temperature. The solution was then warmed to room temperature, and after complete formation of the carbonylimidazolide, propargyl amine (1.00 equiv) was added and the mixture stirred at room temperature for ca. 2 h until the reaction was complete. The product was isolated by filtration, washed with cold water, and dried in vacuo to give a white solid.

*Characterization Data for **2a**.* Yield: 1.4 g, 10.3 mmol, 51%. Mp: 178−184 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): 6.32 (t, $^3J_{HH}$ = 5.8 Hz, 2H, NH), 3.78 (dd, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH}$ = 2.5 Hz, 4H, CH_2), 3.04 (t, $^4J_{HH}$ = 2.5 Hz, 2H, ≡CH). ^{13}C NMR (126 MHz, DMSO-d_6, 298 K): 156.9 (s), 82.3 (s), 72.5 (s), 28.8 (s). HRMS (EI$^+$): *m/z* calculated for [M]$^+$ [$C_7H_9N_2O$]$^+$ 137.0715, found 137.0711.

*Characterization Data for **2b**.* Yield: 1.7 g, 9.0 mmol, 91%, Mp: 117−120 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): 7.29−7.17 (m, 5H, Ph-H), 6.39 (t, $^3J_{HH}$ = 5.4 Hz, 1H, NH), 6.20 (t, $^3J_{HH}$ = 5.4 Hz, 1H, NH), 4.22 (d, $^3J_{HH}$ = 5.9 Hz, 2H, CH_2), 3.82 (m, 2H, CH_2), 2.81 (s, 1H, ≡CH). ^{13}C NMR (126 MHz, DMSO-d_6, 298 K): 157.4 (s), 140.3 (s), 127.9 (s), 126.9 (s), 126.4 (s), 82.0 (s), 71.9 (s), 42.9 (s), 28.8 (s). HRMS (EI$^+$): *m/z* calculated for [M]$^+$ [$C_{11}H_{12}N_2O$]$^+$ 188.0950, found 188.0941.

Synthesis of 3. *General Procedure.* Propargyl carbamates were synthesized by the following method. Carbamoyl chloride (1.00 equiv) and DMAP (0.05 equiv) were added to a solution of propargyl alcohol (1.00 equiv) in pyridine (5 mL), and the resulting mixture was heated overnight at 80 °C. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were then washed further with saturated NH_4Cl solution (3 × 20 mL), dried over sodium sulfate, and filtered, and the solvent was removed in vacuo.

*Characterization Data for **3a**.* Purification by column chromatography gave a colorless oil (SiO_2, PE/EA 95/5). Yield: 0.35 g, 1.64 mmol, 67%. R_f = 0.44 (PE/EA 80/20). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 4.70 (d, $^4J_{HH}$ = 2.5 Hz, 2H), 4.92 (br s, 2H), 2.42 (t, $^4J_{HH}$ = 2.5 Hz, 1H), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): 154.8 (s), 79.1 (s), 74.1 (s), 52.2 (s), 46.2 (br s), 21.1 (br s). IR (ATR) (cm^{-1}): ν_{max} 3247, 2971, 1702, 1443, 1370, 1310, 1294, 1219, 1160, 1136, 1069, 960, 771, 719, 624, 606. MS-EI: 183.1 (13), 169.1 (11), 168.1 (100), 161.9 (6), 151.0 (6), 126.1 (39), 102.1(5), 82.1 (11), 70.0 (11). HRMS (EI$^+$): *m/z* calculated for [M + H]$^+$ [$C_{10}H_{17}NO_2$]$^+$ 183.1259, found 183.1239.

*Characterization Data for **3b**.* Purification by column chromatography gave a colorless oil (SiO_2, PE/EA 95/5). Yield: 0.61 g, 3.10 mmol, 62%. R_f = 0.33 (PE/EE 95/5). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 5.42 (dq, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 2.1 Hz, 1H), 4.28−3.55 (m, 2H), 2.40 (d, $^4J_{HH}$ = 2.1 Hz, 1H), 1.50 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.21−1.18 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): 154.6 (s), 83.3 (s), 72.3 (s), 60.2 (s), 46.0 (br s), 21.8 (s), 21.1 (br s). IR (cm^{-1}): ν_{max} 3312, 3248, 2972, 2937, 2876, 2121, 1694, 1437, 1370, 1344, 1319, 1284, 1210, 1191, 1158, 1133, 1091, 1045, 918, 768, 661. MS ESI: 197.1 (31), 183.1 (12), 182.1 (100), 161.9 (5), 150.9 (5), 138.1 (5), 130.0 (35), 128.1 (11), 102.0 (11), 96 (18), 88.0 (17), 86.1 (23), 86.0 (19). HRMS (EI$^+$): *m/z* calculated for [M + H]$^+$ [$C_{11}H_{19}NO_2$]$^+$ 197.1416, found 197.1422.

*Characterization Data for **3c**.* Purification by recrystallization from petroleum ether 40−60 with a few drops of Et_2O to solubilize the solid at −40 °C gave a pale yellow solid. Yield: 1.07 g, 4.26 mmol, 71%. Mp: 128−133 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 7.28−7.13 (m, 10H, Ph-H), 4.68 (s, 2H, CH_2), 2.37 (s, 1H, ≡CH). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 154.1 (s), 142.4 (s), 129.1 (s), 127.1 (s), 126.5 (s), 78.2 (s), 74.9 (s), 53.5 (s). IR (cm^{-1}): ν_{max} 3087, 3062, 3027, 2950, 2922, 2870, 1944, 1861, 1803, 1730, 1605, 1495, 1461, 1379, 1304, 1210, 1180, 1083, 1059, 1031, 896, 735. HRMS (AP$^+$): *m/z* calculated for [M + H]$^+$ [$C_{16}H_{14}NO$]$^+$ 252.1025, found 252.1017.

Synthesis of 4. The propargyl carbamate was synthesized by the following method. Propargylamine (0.51 mL, 8 mmol) was added to a solution of chloroformate (1.2 mL, 8 mmol) and $NaHCO_3$ (0.67 g, 8 mmol) in 10 mL of EtOH/H_2O (1/1) at 0 °C. The solution was warmed to room temperature and stirred overnight. The solution was diluted with EtOH/H_2O and the aqueous phase extracted with diethyl ether (3 × 20 mL). The combined organic phases were then washed with saturated NH_4Cl solution (3 × 20 mL), dried over sodium sulfate, and filtered, and the solvent was removed in vacuo. The crude product was purified by recrystallization from petroleum ether 40−60 with a few drops of Et_2O to solubilize the solid left at −40 °C. Yield: 1.48 g, 7.82 mmol, 98%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 7.36 (m, 5H, Ph-H), 5.13 (s, 2H, CH_2-O), 4.98 (br s, 1H, NH), 4.00 (s, 2H, N-CH_2), 2.24 (t, $^4J_{HH}$ = 2.5 Hz, 1H, ≡CH). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 156.0 (s), 136.2 (s), 128.6 (s), 128.3 (m), 127.1 (s), 79.8 (s), 71.7 (s), 67.2 (s), 30.9 (s). IR (cm^{-1}): υ_{max}= 3421, 3308, 3087, 3064, 3030, 2982, 2922, 2875, 2739, 2123, 1950, 1864, 1811, 1732, 1606, 1511, 1457, 1381, 1353, 1325, 1227, 1176, 1141, 1085, 1047, 987, 939, 908, 870, 775. HRMS (EI$^+$): *m/z* calculated for [M]$^+$ [$C_{11}H_{11}NO_2$]$^+$ 189.0785, found 189.0790.

Synthesis of 5a. *n*-Butyllithium (2.00 mL, 2.5 M in hexane, 5.00 mmol) was added to a solution of 1-pentyn-3-ol (0.43 mL, 5.00 mmol) in THF (10−20 mL) at −78 °C and the resulting solution stirred for 1 h. Diethyl pyrocarbonate (0.73 mL, 5.00 mmol) in 20 mL of THF was then added to the cooled solution and the mixture warmed to room temperature and subsequently stirred for 12−24 h. The reaction mixture was quenched with saturated NH_4Cl solution (20 mL) and the aqueous phase extracted with diethyl ether (3 × 20 mL). The combined organic phases were then washed with saturated NH_4Cl solution (3 × 20 mL), dried over $NaSO_4$, and filtered, and the solvent was removed in vacuo. The product was purified by column chromatography using SiO_2 (PE/EE, 95/5 to 80/20) to give the pure product. Yield: 0.57 g, 3.65 mmol, 73%. R_f = 0.44 (PE/EE 95/5). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 5.09 (dt, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, CH), 4.22 (q, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 2.50 (d, $^4J_{HH}$ = 1.3 Hz, 1H, ≡CH), 1.88−1.81 (m, 2H, CH_2), 1.32 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3), 1.04 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): 154.7 (s), 80.8 (s), 74.7 (d), 69.0 (d), 64.7 (t), 28.2 (t), 14.6 (q), 9.5 (q). IR (cm^{-1}): ν_{max} 3293, 2979, 2940, 2882, 2358, 2125, 1756, 1515, 1465, 1396, 1373, 1342, 1302, 1275, 1177, 1094, 1062, 1046, 1007, 948, 932, 893, 857, 791, 670. MS-EI: 128.0 (39), 127.0 (8), 91.0 (12), 84.1 (7), 83.1 (51), 69.0 (30), 67.1 (82), 66.0 (100), 63.0 (20). HRMS (EI$^+$): *m/z* calculated for [M − C_2H_4]$^+$ [$C_6H_8O_3$]$^+$ 128.0473, found 128.0487.

Synthesis of 5b. Propargyl carbonate **5b** was synthesized according to a similar literature method.[28] Propargyl alcohol (1.7 mL, 30 mmol) was dissolved in dichloromethane in combination with Hünig's base (13.1 mL, 75 mmol) alongside DMAP (10 mol %). After the mixture was cooled to 0 °C, Boc anhydride (8.51 g, 39 mmol) was added portionwise, ensuring the reaction mixture was not allowed to reflux, and then stirred until completion. The resultant solution was quenched with saturated NH_4Cl solution (20 mL) and the aqueous phase extracted with dichloromethane (3 × 20 mL). The combined organic phases were then washed with 1 M HCl, saturated $NaHCO_3$ solution, and brine (all 2 × 20 mL), dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo to give a colorless oil. The product was sufficiently pure for subsequent reactions. Yield: 3.4 g, 21.8 mmol, 73%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 2.53 (s, 1H, ≡CH), 1.68 (s, 6H, CH_3), 1.48 (s, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): 151.5 (s), 84.6 (s), 82.4 (s), 73.0 (s), 72.5 (s), 29.0 (s), 28.0 (s).

Synthesis of 6. *General Procedure.* To a solution of alcohol (3.00 mmol, 1.00 equiv) in CH_2Cl_2 were added NEt_3 (3.00 mmol, 1.00 equiv) and DMAP (2 mol %), and the solution was cooled to 0 °C.

DOI: 10.1021/acs.organomet.5b00753
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For **6a**,**b** diphenylphosphoryl chloride (3.00 mmol, 1.00 equiv) or for **6c**,**d** diphenylphosphinoyl chloride (3.00 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (20 mL) and was added at this temperature. The solution was stirred for 1 h and slowly warmed to room temperature and stirred overnight. Water (20 mL) was added, the phases were separated, and the aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. The products were sufficiently pure for subsequent reactions.

*Characterization Data for **6a**.* Yield: 0.92 g, 3.00 mmol, quant. R_f = 0.34 (PE/EA 80/20) ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 7.28−7.24 (m, 4H), 7.20−7.08 (m, 6H), 5.27−5.18 (m, 1H), 2.49 (d, $^4J_{HH}$ = 2.1 Hz, 1H), 1.50 (d, $^3J_{HH}$ = 6.62 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): 150.6 (d, J_{PC} = 7.6 Hz), 150.5 (d, J_{PC} = 7.3 Hz), 129.9 (d, J_{PC} = 0.9 Hz), 129.8 (d, J_{PC} = 0.9 Hz), 125.5 (d, J_{PC} = 1.5 Hz), 125.5 (d, J_{PC} = 1.3 Hz), 120.3 (d, J_{PC} = 4.9 Hz, 2C), 120.3 (d, J_{PC} = 4.8 Hz), 81.2 (d, J_{PC} = 6.0 Hz), 75.1 (s), 65.9 (d, J_{PC} = 5.6 Hz), 23.3 (d, J_{PC} = 6.1 Hz). ^{31}P NMR (120 MHz, $CDCl_3$, 298 K): −12.8 (s). IR (ATR) (cm^{-1}): ν_{max} 3282, 2126, 1718, 1593, 1492, 1457, 1291, 1220, 1196, 1168, 1092, 1029, 999, 967, 916, 781, 693, 656, 617. MS EI: 302.0 (100), 292.9 (22), 251.0 (25), 250.0 (84), 249.0 (79), 209.0 (67), 170.0 (41), 145.0 (14), 129.0 (15), 128.0 (55), 94.0 (89). HRMS (EI$^+$): m/z calculated for $[M]^+$ $[C_{16}H_{15}O_4P]^+$ 302.0708, found 302.0692.

*Characterization Data for **6b**.* Yield: 1.65 g, 5.0 mmol, quant. R_f = 0.43 (PE/EA 80/20). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 7.15−6.94 (m, 10H), 5.14−5.05 (m, 1H), 1.94 (qd, $^3J_{HH}$ = 6.6 Hz, $^5J_{HH}$ = 1.95 Hz, 2H), 1.33 (d, $^3J_{HH}$ = 7.5 Hz, 3H), 0.86 (t, $^3J_{HH}$ = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): 150.7 (d, J_{PC} = 7.5 Hz), 150.6 (d, J_{PC} = 7.4 Hz), 129.8 (d, J_{PC} = 0.5 Hz), 129.7 (d, J_{PC} = 0.5 Hz), 125.4 (d, J_{PC} = 1.2 Hz), 125.3 (dd, J_{PC} = 1.3 Hz), 120.3 (dd, J_{PC} = 3.8 Hz), 120.3 (d, J_{PC} = 3.8 Hz), 89.3 (s), 77.3 (d, J_{PC} = 5.6 Hz), 67.0 (d, J_{PC} = 5.7 Hz), 23.8 (d, J_{PC} = 6.4 Hz), 13.5 (s), 12.4 (s). ^{31}P NMR (120 MHz, $CDCl_3$, 298 K): −12.8 (s). IR (cm^{-1}): ν_{max} 2976, 2937, 2878, 2247, 1694, 1592, 1490, 1437, 1370, 1346, 13178, 1286, 1221, 1192, 1163, 1133, 1105, 1071, 1058, 1047, 1010, 989, 956, 901, 802, 769, 689, 616. MS EI: 330.1 (56), 252.0 (14), 251.0 (100), 250.0 (76), 249.0 (38), 238.0 (6), 237.0 (48), 170.0 (20), 161.9 (6), 150.9 (7), 94.0 (39), 81.0 (7), 80.0 (9), 79.0 (15), 77.0 (15). HRMS (EI$^+$): m/z calculated for $[M]^+$ $[C_{18}H_{19}O_4P]^+$ 330.1021, found 330.1019.

*Characterization Data for **6c**.* Yield: 0.81 g, 3.0 mmol, quant. R_f = 0.32 (PE/EA 50:50). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 7.89−7.76 (m, 4H), 7.53−7.38 (m, 6H), 5.20−5.10 (m, 1H), 2.43 (d, $^4J_{HH}$ = 2.1 Hz, 1H), 1.62 (d, $^3J_{HH}$ = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): 132.3 (d, J_{PC} = 58.2 Hz), 132.3 (d, J_{PC} = 2.9 Hz), 132.2 (d, J_{PC} = 2.8 Hz), 132.1 (dd, J_{PC} = 10.4 Hz), 131.4 (d, J_{PC} = 2.9 Hz), 130.6 (d, J_{PC} = 52.6 Hz), 128.6 (d, J_{PC} = 13.4 Hz), 128.4 (d, J_{PC} = 13.2 Hz), 82.5 (d, J_{PC} = 6.1 Hz), 74.0 (s), 61.7 (d, J_{PC} = 5.2 Hz), 24.2 (d, J_{PC} = 3.8 Hz). ^{31}P NMR (120 MHz, $CDCl_3$, 298 K): 32.7 (s). IR ATR (cm^{-1}): υ_{max}= 3392, 3067, 2981, 2936, 2245, 1593, 1440, 1375, 1343, 1321, 1231, 1167, 1131, 1115, 1072, 1053, 1007, 967, 926, 798, 758, 734, 704, 674, 641, 629, 617. MS EI: 270.0 (100), 269.0 (9), 241.0 (12), 217.0 (12), 203.0 (16), 202.0 (41), 201.0 (63), 199.0 (14), 155.0 (7), 146.0 (7), 141.0 (7), 129.0 (11), 77.0 (30). HRMS (EI$^+$) m/z calculated for $[M]^+$ $[C_{16}H_{15}O_2P]^+$: 270.0810, found: 270.0805.

*Characterization Data for **6d**.* Yield: 0.92 g, 3.0 mmol, quant. R_f = 0.33 (PE:EE = 50/50). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 7.92−7.76 (m, 4H), 7.54−7.39 (m, 6H), 5.24−5.14 (m, 1H), 2.05 (qd, $^3J_{HH}$ = 7.5 Hz, $^5J_{HH}$ = 1.92 Hz, 2H), 1.58 (d, $^3J_{HH}$ = 6.5 Hz, 3H), 0.98 (t, $^3J_{HH}$ = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): 132.4 (d, J_{PC} = 58.2 Hz), 132.2 (d, J_{PC} = 10.4 Hz), 132.0 (d, J_{PC} = 2.6 Hz), 132.0 (d, J_{PC} = 2.8 Hz), 131.3 (d, J_{PC} = 10.3 Hz), 130.1 (d, J_{PC} = 51.4 Hz), 128.4 (d, J_{PC} = 13.3 Hz), 128.3 (d, J_{PC} = 13.1 Hz), 88.3 (s), 78.4 (d, J_{PC} = 5.3 Hz), 62.5 (d, J_{PC} = 5.4 Hz), 24.5 (d, J_{PC} = 4.5 Hz), 13.4 (s), 12.3 (s). ^{31}P NMR (120 MHz, $CDCl_3$, 298 K): 31.9 (s). IR ATR (cm^{-1}): ν_{max} 3299, 3194, 2993, 2115, 1594, 1487, 1455, 1436, 1375, 1352, 1310, 1211, 1179, 1162, 1132, 1114, 1087, 1013, 970, 854, 787, 756, 728, 695, 675. MS (EI): 298.1 (100), 283.0 (62), 269.0 (12), 219.0 (91), 202.0 (43), 201.0 (65), 143.0 (17), 141.0 (16), 77.0 (28). HRMS (EI$^+$): m/z calculated for $[M]^+$ $[C_{18}H_{19}O_2P]^+$ 298.1123, found 298.1130.

Synthesis of 7a. 3,4-Dimethoxy-*N*,*N*-di(prop-2-yn-1-yl)-benzamide (**1a**; 52 mg, 0.2 mmol) was dissolved in toluene (2 mL) and added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. After 1 h small crystals formed, which were redissolved by briefly warming the solution slightly and adding a few drops of CH_2Cl_2. Upon cooling large colorless blocks of the adduct formed which were suitable for X-ray diffraction. The crystals were washed with petroleum ether 40−60 (3 × 3 mL) to give the adduct **7a**. Yield: 119 mg, 0.15 mmol, 77%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 7.2−7.1 (m, ca. 2H, tol), 6.70 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.9 Hz, 1H), 6.63 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 6.50 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 4.64 (br s, 2H), 4.17 (d, $^4J_{HH}$ = 2.3 Hz, 2H), 3.79 (s, 3H), 3.61 (s, 3H), 2.46 (t, $^4J_{HH}$ = 2.3 Hz, 1H), 2.40 (t, $^4J_{HH}$ = 2.4 Hz, 1H), 2.28 (s, ca. 1.2H, tol). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): 0.5 (br s). ^{19}F NMR (283 MHz, $CDCl_3$, 298 K): −133.6 (d, $^3J_{FF}$ = 20.6 Hz, 2F, *o*-F), −157.5 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-F), −164.1 (m, 2F, *m*-F). The product could not be fully characterized in solution, as subsequent dissociation of boron from the amide oxygen atom followed by cyclization to yield **8a** occurs. Anal. Calcd for $C_{33}H_{15}BF_{15}NO_3$: C, 51.52; H, 1.97; N, 1.82. Found: C, 51.49; H, 1.85; N, 1.82. IR (cm^{-1}): ν_{max} 2359, 2340, 2322, 1647, 1560, 1560, 1516, 1464, 1456, 1273, 1258, 1240, 1099, 978.

Synthesis of 7b. 3-Methyl-*N*,*N*-di(prop-2-yn-1-yl)but-2-enamide (**1b**; 36 mg, 0.2 mmol) was dissolved in toluene (ca. 2 mL) and added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction mixture was left at room temperature without stirring for 30 min. Slow evaporation of the solvent yielded large colorless blocks of the product which could be characterized by X-ray diffraction. The remaining solvent was decanted off and the product washed with petroleum ether (3 × 3 mL) and dried in vacuo to give pure **7b.** Yield: 57 mg, 0.08 mmol, 41%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 7.12−6.95 (m, ca. 2H, tol), 5.32 (br s, 1H), 4.49 (d, $^4J_{HH}$ = 2.2 Hz, 2H), 4.28 (d, $^4J_{HH}$ = 2.2 Hz, 2H), 2.38 (t, $^4J_{HH}$ = 2.2 Hz, 1H), 2.24 (t, $^4J_{HH}$ = 2.2 Hz, 1H), 2.19 (s, ca. 1.4H, tol), 1.48 (s, 3H), 1.24 (s, 3H). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −0.5 (br s). ^{19}F NMR (283 MHz, $CDCl_3$, 298 K): −134.1 (d, $^3J_{FF}$ = 20.1 Hz, 2F, *o*-F), −157.4 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-F), −164.0 (m, 2F, *m*-F). The product could not be fully characterized in solution, as subsequent dissociation of boron from the amide oxygen atom followed by cyclization to yield **8b** occurs. Anal. Calcd for $C_{29}H_{13}BF_{15}NO$: C, 50.68; H, 1.91; N, 2.04. Found: C, 50.83; H, 1.82; N, 2.11. IR (cm^{-1}): ν_{max} 2361, 2340, 2322, 1647, 1559, 1516, 1456, 1281, 1257, 1092, 980, 868, 806, 766, 729, 690, 682.

Synthesis of 8a. 3,4-Dimethoxy-*N*,*N*-di(prop-2-yn-1-yl)-benzamide (**1a**; 52 mg, 0.2 mmol) was dissolved in toluene (8 mL) and added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction mixture was heated to 45 °C for 2 days without stirring, whereupon CH_2Cl_2 (ca. 0.5 mL) was added. Upon cooling small colorless crystals of the product formed. The remaining solvent was decanted off, and the crystals were washed with petroleum ether (3 × 3 mL) and then dried under vacuum to give colorless crystals of the pure product. Yield: 89 mg, 0.12 mmol, 58%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 7.59 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.2 Hz, 1H), 7.35 (d, $^4J_{HH}$ = 2.2 Hz, 1H), 7.10 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 6.64 (br s, 1H), 4.54 (d, $^4J_{HH}$ = 2.6 Hz, 2H), 4.38 (d, $^4J_{HH}$ = 2.6 Hz, 2H), 4.04 (s, 3H), 3.98 (s, 3H), 2.75 (t, $^4J_{HH}$ = 2.2 Hz, 1H). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −16.9 (s). ^{19}F NMR (283 MHz, $CDCl_3$, 298 K): −132.7 (d, $^3J_{FF}$ = 22.4 Hz, 2F, *o*-F), −160.8 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-F), −165.0 (m, 2F, *m*-F). Anal. Calcd for $C_{33}H_{15}BF_{15}NO_3$: C, 51.52; H, 1.97; N, 1.82. Found: C, 51.50; H, 1.89; N, 1.91. IR (cm^{-1}): ν_{max} 2357, 2342, 1613, 1597, 1512, 1458, 1437, 1396, 1348, 1284, 1271, 1080, 961, 810, 768.

Synthesis of 8b. 3-Methyl-*N*,*N*-di(prop-2-yn-1-yl)but-2-enamide (**1b**; 36 mg, 0.2 mmol) was dissolved in toluene (8 mL) and added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction mixture was heated to 45 °C for 2 days without stirring, giving an orange solution. Upon cooling small colorless acicular crystals of the product formed. The remaining solvent was decanted off, and the crystals were washed with petroleum ether (3 × 3 mL) and dried under vacuum to give colorless crystals of the pure product. Yield: 79 mg, 0.11 mmol, 57%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 6.53 (br s,

DOI: 10.1021/acs.organomet.5b00753
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2H), 5.96 (br s, 1H), 4.32 (d, $^4J_{HH}$ = 2.4 Hz, 2H), 4.15 (d, $^4J_{HH}$ = 2.4 Hz, 2H), 2.62 (t, $^4J_{HH}$ = 2.5 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −16.9 (s). ^{19}F NMR (283 MHz, $CDCl_3$, 298 K): −132.7 (d, $^3J_{FF}$ = 21.9 Hz, 2F, *o*-F), −160.9 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-F), −165.1 (m, 2F, *m*-F). HRMS (EI$^+$): *m*/*z* calculated for [M − H]$^-$ [$C_{29}H_{12}BF_{15}NO$]$^-$ 686.0772, found 686.0799. IR (cm^{-1}): ν_{max} 2359, 2334, 2322, 1636, 1512, 1456, 1271, 1262, 1080, 974, 963, 806.

Synthesis of 8c. 4-Nitro-*N*,*N*-di(prop-2-yn-1-yl)benzamide (**1c**; 48 mg, 0.2 mmol) was dissolved in toluene (3 mL) and was added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction mixture was left at room temperature for 1 h, CH_2Cl_2 (ca. 1 mL) was added, and the solvent was allowed to evaporate slowly to give small acicular colorless crystals of the product which were suitable for X-ray diffraction. The remaining solvent was decanted off, and the crystals were washed with petroleum ether (3 × 3 mL) and then dried under vacuum to give colorless crystals of the pure product. Yield: 130 mg, 0.17 mmol, 86%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.51 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 8.08 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.69 (s, 1H, CH), 5.23 (s, 2H), 4.47 (br d, $^4J_{HH}$ = 2.4 Hz, 2H), 2.78 (t, $^4J_{HH}$ = 2.4 Hz, 1H). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −16.9 (s). ^{19}F NMR (283 MHz, $CDCl_3$, 298 K): −132.7 (d, $^3J_{FF}$ = 22.5 Hz, 2F, *o*-F), −160.3 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-F), −164.7 (m, 2F, *m*-F). Anal. Calcd for $C_{31}H_{10}BF_{15}N_2O_3$: C, 49.37; H, 1.34; N, 3.7. Found: C, 52.50; H, 1.64; N, 3.52. IR (cm^{-1}): ν_{max} 2361, 2341, 1653, 1636, 1597, 1533, 1512, 1456, 1445, 1400, 1358, 1296, 1267, 1258, 1084, 978, 961, 928, 891, 866, 808, 770, 739, 716, 692, 669.

Synthesis of 8d. *N*,*N*-Di(prop-2-yn-1-yl)cyclohexanecarboxamide (**1d**; 40 mg, 0.2 mmol) was dissolved in toluene (2 mL) and added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give a cloudy yellow solution. Leaving the solution to stand for 10 min resulted in the formation of a white precipitate, which was redissolved by gentle heating with the addition of a few drops of CH_2Cl_2. The reaction mixture was left for 2 days, and then the solvent was allowed to evaporate slowly to give colorless crystals of the product which were suitable for X-ray diffraction. The remaining solvent was decanted off, and the crystals were washed with petroleum ether (3 × 3 mL) and then dried under vacuum to give colorless crystals of the pure product. Yield: 114 mg, 0.15 mmol, 80%. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): 6.31 (s, 1H, =CH), 4.51 (s, 2H, CH_2), 4.06 (s, 2H, CH_2), 2.78 (t, $^4J_{HH}$ = 2.5 Hz, 1H, ≡CH), 1.90−1.68 (m, 5H, CH), 1.53−1.45 (m, 2H, CH), 1.33−1.17 (m, 4H, CH). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −17.0 (s). ^{19}F NMR (283 MHz, $CDCl_3$, 298 K): −132.8 (d, $^3J_{FF}$ = 22.4 Hz, 2F, *o*-F), −160.9 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-F), −165.3 (m, 2F, *m*-F). Anal. Calcd for $C_{31}H_{17}BF_{15}NO$: C, 52.06; H, 2.40; N, 1.96. Found: C, 51.94; H, 2.24; N, 1.94. HRMS (EI$^+$): *m*/*z* calculated for [M]$^+$ [$C_{31}H_{16}BF_{15}NO$]$^+$ 714.1085, found 714.1079. IR (cm^{-1}): ν_{max} 2363, 2342, 2322, 1630, 1512, 1454, 1437, 1304, 1260, 1233, 1180, 1138, 1113, 1078, 978, 961, 883, 841, 818, 806, 768, 669.

Synthesis of 9a. $B(C_6F_5)_3$ (51 mg, 0.1 mmol) was dissolved in $CDCl_3$ (ca. 0.5 mL) and added to 1,3-di(prop-2-yn-1-yl)urea **2a** (14 mg, 0.1 mmol). The reaction mixture was heated at 50 °C for 7 days to give a yellow solution and a crop of needle-shaped crystals which were suitable for X-ray diffraction. The remaining solvent was decanted off, and the product was washed with hexane (4 × 2 mL) and dried in vacuo to give pure **9a**. Yield: 20 mg, 0.03 mmol, 31%. Mp: 178−184 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): 10.01 (br s, 1H, NH), 5.91 (s, 1H, NH), 5.65 (s, 1H, =CH), 4.07 (d, $^4J_{HH}$ = 2.0 Hz, 2H, CH_2), 3.64 (s, 2H, CH_2), 3.30 (br s, 1H, CH). ^{11}B NMR (160 MHz, DMSO-d_6, 298 K): −17.0 (s). ^{19}F NMR (283 MHz, DMSO-d_6, 298 K): 132.1 (d, $^3J_{FF}$ = 22.2 Hz, 2F, *o*-F), 161.3 (t, $^3J_{FF}$ = 22.2 Hz, 1F, *p*-F), 165.2 (t, $^3J_{FF}$ = 22.2 Hz, 2F, *m*-F). IR (cm^{-1}): ν_{max} 3085, 3061, 3029, 2922, 2876, 1708, 1672, 1643, 1607, 1572, 1545, 1514, 1495, 1460, 1380, 1280, 1082, 1030, 977, 729, 695. HRMS (ES$^-$): *m*/*z* calculated for [M − H]$^-$ [$C_{25}H_7BN_2OF_{15}$]$^-$ 646.0448, found 646.0445.

Synthesis of 9b. $B(C_6F_5)_3$ (51 mg, 0.1 mmol) was dissolved in $CDCl_3$ (ca. 0.5 mL) and added to 1-benzyl-3-(prop-2-yn-1-yl)urea (**2b**; 19 mg, 0.1 mmol). The reaction mixture was heated to 50 °C for 14 days to give a pale yellow solution. The solvent was removed in vacuo, leaving a white solid, which was recrystallized from hexane with a drop of toluene at −40 °C to give colorless crystals of **9b**. Yield: 43 mg, 0.06 mmol, 31%. Mp: 182−190 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): 10.11 (br s, 1H, NH), 7.39−7.30 (m, 5H, Ph-H), 5.90 (br s, 1H, NH), 5.74 (s, 1H, =CH), 4.43 (br s, 2H, CH_2), 3.65 (br s, 2H, CH_2). ^{11}B NMR (160 MHz, DMSO-d_6, 298 K): −16.9 (br s). ^{19}F NMR (283 MHz, DMSO-d_6, 298 K): −132.1 (d, $^3J_{FF}$ = 21.3 Hz, 2F, *o*-F), −161.1 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*-F), −165.1 (t, $^3J_{FF}$ = 21.0 Hz, 2F, *m*-F). IR (cm^{-1}): ν_{max} 3088, 3062, 3029, 2923, 2783, 1944, 1865, 1808, 1648, 1605, 1519, 1495, 1469, 1380, 1287, 1101, 1067, 1032, 981, 872, 819, 771, 733, 695, 616. HRMS (ES$^-$): *m*/*z* calculated for [M − H]$^-$ [$C_{29}H_{11}BN_2OF_{15}$]$^-$ 698.0761, found 698.0790.

Synthesis of 10a. Prop-3-yn-2-yldiisopropylcarbamate (**3a**; 18.3 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol) were dissolved in 0.6 mL of CD_2Cl_2, and the mixture was left for 24 h. The progress of the reaction was monitored by ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The solution was concentrated and, when the reaction was complete, layered with pentane and stored at −20 °C, whereby the product crystallized out. The remaining solution was decanted off and the resulting solid washed with cold pentane (3 × 2 mL). Drying in vacuo afforded the product as a white crystalline solid. Yield: 44.5 mg, 0.06 mmol, 64%. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): 6.46 (s, 1H, CH), 4.85 (d, $^4J_{HH}$ = 2.1 Hz, 2H), 4.22 (sept., $^3J_{HH}$ = 6.9 Hz, 1H), 4.07 (sept., $^3J_{HH}$ = 6.9 Hz, 1H), 1.39 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.36 (d, $^3J_{HH}$ = 6.9 Hz, 6H). ^{11}B NMR (96 MHz, CD_2Cl_2, 298 K): −17.0 (s). ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K): −133.0 (d, $^3J_{FF}$ = 22 Hz, 6F, *o*-F $B(C_6F_5)_3$), −161.9 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-F $B(C_6F_5)_3$), −166.2 (m, 6F, m-F $B(C_6F_5)_3$). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): 160.9 (s), 148.7 (dm), 140.5 (m), 139.1 (dm), 137.2 (dm), 123.4 (br s), 119.4 (q), 74.1 (s), 71.6 (s), 53.0 (s), 51.7 (s), 20.2 (s), 20.2 (s). IR (ATR) (cm^{-1}): ν_{max} 1716, 1663, 1643, 1512, 1457, 1442, 1404, 1379, 1363, 1264, 1144, 1079, 1066, 978, 959, 902, 867, 844, 804, 763, 747, 736, 704, 675, 658, 642, 607. MS-DART: 696.1 (30), 684.2 (25), 681.4 (28), 680.4(64), 610.1,(35), 563.1 (28), 550.5 (24), 546.1 (58), 536.1 (26), 528.1 (58). HRMS-DART: (+) *m*/*z* calculated for [M + H]$^+$ [$C_{28}H_{18}BF_{15}NO_2$]$^+$ 696.1191, found 696.1183.

Synthesis of 10c. Prop-2-yn-1-yldiphenylcarbamate (**3c**; 50 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102 g, 0.2 mmol) were dissolved in 2 mL of toluene to give a clear colorless solution. This was immediately cooled to −40 °C and left for 5 days to give a crop of small pale yellow crystals suitable for X-ray diffraction. The solution was decanted, and the solid was washed with hexane (3 × 2 mL) and dried in vacuo to afford the product as a white solid. Yield: 91 mg, 0.12 mmol, 60%. Mp: 65−72 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 7.46−7.25 (m, 10H, Ph-H), 6.43 (s, 1H, =CH), 4.9 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 162.3 (s), 149.2 (m), 147.3 (m), 139.9 (m), 140.3 (s), 147.3 (m), 139.9 (m), 137.9 (m), 135.9 (m), 130.1 (s), 129.9 (s), 126.7 (m), 126.6 (m), 110.2 (s), 73.0 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K), −17.1 (s). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −132.6 (d, $^3J_{FF}$ = 21.3 Hz, 2F, *o*-F), −160.5 (t, $^3J_{FF}$ = 21.2 Hz, 1F, *p*-F), −164.9 (t, $^3J_{FF}$ = 21.2 Hz, 2F, *m*-F). IR (cm^{-1}): ν_{max} 3088, 3046, 3016, 2915, 2873, 2739, 1946, 1861, 1806, 1737, 1616, 1584, 1518, 1476, 1381, 1319, 1287, 1251, 1212, 1179, 1101, 1088, 1029, 973, 898, 774, 739, 719, 702, 689. HRMS (EI$^-$): *m*/*z* calculated for [M − H]$^-$ [$C_{34}H_{12}BNO_2F_{15}$]$^-$ 761.0785, found 761.0775.

Synthesis of 11a. Prop-3-yn-2-yldiisopropylcarbamate (**3a**; 18 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol) were dissolved in 0.6 mL of C_6D_6, and the reaction mixture was left at 60 °C for 15.5 h. The progress of the reaction was monitored by ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The solution was concentrated when the reaction was complete and layered with pentane and then stored at −20 °C, whereby the product crystallized out. The remaining solution was decanted off and the resulting solid washed with cold pentane (3× 2 mL). Drying in vacuo afforded the product as a white crystalline solid. Yield: 50.4 mg, 0.07 mmol, 72%. ^{1}H NMR (600 MHz, C_6D_6 298 K): 4.68 (s, 1H), 4.55 (d, $^4J_{HH}$ = 2.6 Hz, 1H), 4.48 (br s, 1H), 4.38 (d, $^4J_{HH}$ = 2.6 Hz, 1H), 3.06 (br s, 1H), 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 0.86 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.83 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 0.80 (d, $^3J_{HH}$ = 6.8 Hz, 3H). ^{11}B NMR (96 MHz, C_6D_6, 298 K): 0.8 (br s). ^{19}F NMR (282 MHz, C_6D_6, 298 K): −134.8 (br d, 2F, *o*-F, $B(C_6F_5)_2$), −136.0 (m, 2F,

DOI: 10.1021/acs.organomet.5b00753
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o-F, $B(C_6F_5)_2$), −143.0 (m, 2F, *o*-F C_6F_5), −156.8 (m, 2F, *p*-F, $B(C_6F_5)_2$), −157.6 (t, $^3J_{FF}$ = 21.7 Hz, 1F, *p*-F, C_6F_5), −162.9 (br s, 2F, *m*-F, C_6F_5), −163.4 (m, 2F, *m*-F, $B(C_6F_5)_2$), −163.7 (m, 2F, *m*-F $B(C_6F_5)_2$). ^{13}C NMR (150 MHz, C_6D_6, 298 K): 156.4 (s), 155.8 (s), 148.4 (dm), 147.9 (dm), 145.3 (dm), 140.38 (dm), 139.3 (dm), 137.7 (dm), 118.9 (br s, C−B), 117.7 (t), 98.9 (s), 49.7 (s), 47.3 (s), 29.0 (br s), 20.6 (s), 20.1 (s), 19.0 (s), 18.9 (s).

Synthesis of 11b. But-3-yn-2-yldiisopropylcarbamate (**3b**; 19.7 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol) were dissolved in 0.6 mL of CD_2Cl_2, and the reaction mixture was left for 24 h. The completion of the reaction was monitored by ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The solution was concentrated when the reaction was complete and layered with pentane and stored at −20 °C, resulting in crystallization of the product. The remaining solution was decanted off, and the solid was washed with cold pentane (3 × 2 mL). Drying in vacuo afforded the product as a white crystalline solid. Yield: 54.7 mg, 0.08 mmol, 75%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): 5.04 (q, $^3J_{HH}$ = 6.9 Hz, 1H, =CH), 4.68−4.64 (m, 1H, CH), 4.34 (s, 1H, CH), 4.00−3.91 (m, 1H, CH), 1.70 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.44−1.30 (m, 12H, CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): 156.7 (s), 149.1 (m), 148.4 (dm), 147.8 (dm), 145.4 (dm), 140.4 (dm), 140.1 (dm), 139.3 (dm) 137.9 (dm), 137.6 (dm), 137.3 (dm), 119.0 (t), 118.4 (br m), 110.2 (s), 50.1 (s), 48.1 (s), 29.4 (br s), 21.1 (s), 20.5 (s), 20.0 (s), 19.8 (s), 11.0 (s). ^{11}B NMR (96 MHz, CD_2Cl_2, 298 K): 0.0 (br s). ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K): −135.0 (br s, 2F, *o*-F $B(C_6F_5)_2$), −136.3 (m, 2F, *o*-F $B(C_6F_5)_2$), −143.1 (d, $^3J_{FF}$ = 20.6 Hz, 2F, *o*-F C_6F_5), −158.7 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-F $B(C_6F_5)_2$), −159.0 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*-F $B(C_6F_5)_2$), −159.7 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-F C_6F_5), −163.9 (m, 2F, *m*-F C_6F_5), −164.8 (m, 2F, *m*-F $B(C_6F_5)_2$), −165.0 (m, 2F, *m*-F $B(C_6F_5)_2$), all C_6F_5 rings are inequivalent. IR (ATR) (cm^{-1}): ν_{max} 2993, 2978, 1702, 1644, 1614, 1517, 1494, 1464, 1393, 1374, 1284, 1250, 1215, 1182, 1157, 1091, 1068, 1039, 993, 974, 956, 934, 904, 873, 860, 824, 777, 751, 737, 720, 699, 686, 663, 629, 617. MS-DART: 728.1 (26), 727.1 (85), 726.1 (20), 680.4 (30), 610.1 (18), 577.1 (23), 560.1 (31), 559.1 (34), 543.1 (24), 542.1 (100), 541.1 (25), 536.1 (19). HRMS-DART: (+) *m*/*z* calculated for $[M + NH_4]^+$ $[C_{29}H_{23}BF_{15}N_2O_2]^+$ 727.1613, found 727.1601.

Synthesis of 11c. Prop-2-yn-1-yldiphenylcarbamate (**3c**; 50 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102 mg, 0.2 mmol) were dissolved in 2 mL of toluene to give a clear colorless solution. After 5 days at room temperature a few drops of CH_2Cl_2 were added and the solvent was left to evaporate to give large pale yellow blocks suitable for X-ray diffraction. The solution was decanted and the solid washed with hexane (3 × 2 mL). This was then dried in vacuo to yield the pure product as a white solid. Yield: 101 mg, 0.13 mmol, 66%. Mp: 137−146 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 7.50−7.35 (m, 10H, Ar−H), 4.73 (d, $^2J_{HH}$ = 2.5 Hz, 1H, =C−H), 4.66 (d, $^2J_{HH}$ = 2.5 Hz, 1H, =C−H), 4.39 (s, 1H, B−C−H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 157.2 (s), 155.6 (s), 130.1 (s), 129.9 (s), 129.4 (s), 129. (s), 126.7 (s), 126.6 (s), 100.5 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) 1.4 (br s). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −134.0 (d, $^3J_{FF}$ = 21.5 Hz, 2F, *o*-F $B(C_6F_5)_2$), −135.5 (d, $^3J_{FF}$ = 21.5 Hz, 2F, *o*-F $B(C_6F_5)_2$), −141.4 (br s, 1F, *o*-F C_6F_5), −143.2 (br s, 1F, *o*-F C_6F_5), −156.6 (t, $^3J_{FF}$ = 21.2 Hz, 1F, *p*-F $B(C_6F_5)_2$), −157.0 (t, $^3J_{FF}$ = 21.2 Hz, 2F, *p*-F $B(C_6F_5)_2$), −161.2 (br s, 1F, *m*-F C_6F_5), −162.0 (br s, 1F, *m*-F C_6F_5), −163.0 (m, 2F, *m*-F $B(C_6F_5)_2$) −163.8 (m, 2F, *m*-F $B(C_6F_5)_2$. All C_6F_5 rings are inequivalent. IR (cm^{-1}): ν_{max} 3055, 2987, 2686, 2359, 2307, 1673, 1647, 1618, 1582, 1519, 1496, 1487, 1465, 1423, 1384, 1289, 1273, 1260, 1209, 1161, 1107, 1092, 1026, 998, 972, 896, 759, 738, 717, 699. HRMS (EI$^+$): *m*/*z* calculated for $[M + Na]^+$ $[C_{34}H_{13}BF_{15}NO_2Na]^+$ 785.0734, found 785.0711.

Synthesis of 12. Under less anhydrous conditions, benzylprop-2-yn-1-ylcarbamate (**4a**; 38 mg, 0.2 mmol) was added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) in 2 mL of toluene to give a slightly yellow solution. After reaction for 4 days at room temperature the solution was concentrated in vacuo, layered with hexane, and left at −40 °C to produce yellow-orange blocks suitable for X-ray diffraction. Yield: 55 mg, 0.09 mmol, 45%. Mp: 95−102 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.29 (br s, 1H, NH), 6.56 (s, 1H, =CH), 2.18 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 157.9 (s), 148.0 (br s), 147.1 (br s), 141.3 (m), 139.3 (m), 138.2 (m), 136.2 (m), 108.8 (s), 53.6 (s), 11.2 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): 0.7 (br s). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −134.7 (m, 2F, *o*-F), −156.8 (m, 1F, *p*-F), −163.7 (s, 2F, *m*-F). IR (cm^{-1}): 3380, 3088, 3062, 3028, 2922, 2873, 1943, 1863, 1806, 1731, 1697, 1674, 1648, 1604, 1519, 1496, 1470, 1379, 1291, 1105, 1085, 1033, 979, 774, 736, 725, 697, 625. HRMS (EI$^-$): *m*/*z* calculated for $[M - H]^-$ $[C_{22}H_4BNO_2F_{15}]^-$ 609.0132, found 609.0142.

Synthesis of 13. Ethyl pent-1-yn-3-ylcarbonate (**5a**; 15.6 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol) were dissolved in 0.6 mL of CD_2Cl_2, and the mixture was left for 66 h at room temperature. The completion of the reaction was monitored by ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. Removal of the solvent in vacuo afforded the crude product as a brown solid. The product was recrystallized by slow evaporation of toluene to yield a small crop of colorless plates. Yield: 53.9 mg, 0.08 mmol, 81%. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): 5.20 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 4.80 (dq, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.4 Hz, 2H), 4.48 (s, 1H), 2.23−2.04 (m, 2H), 1.55 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 0.93 (t, $^3J_{HH}$ = 7.5 Hz, 3H); ^{11}B NMR (96 MHz, CD_2Cl_2, 298 K): −0.9 (br s). ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K): −139.2 (m, 2F, *o*-F, $B(C_6F_5)_2$), −139.8 (m, 2F, *o*-F $B(C_6F_5)_2$), −147.0 (br s, 2F, *o*-F C_6F_5), −161.2 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-F $B(C_6F_5)_2$), −161.7 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-F $B(C_6F_5)_2$), −162.2 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-F C_6F_5), −166.7 (br m, 2F, *m*-F C_6F_5), −168.2 (m, 4F, *m*-F $B(C_6F_5)_2$). ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): 159.4 (s), 148.5 (dm), 147.8 (dm), 145.5 (dm), 140.9 (dm), 140.6 (dm), 139.8 (dm), 138.3 (dm), 138.1 (dm), 137.7 (dm,), 120.6 (s), 117.6 (t), 117.1 (m), 71.8 (s), 27.9 (br s), 18.8 (s), 14.2 (s), 13.6 (s). IR (reflection) (cm^{-1}): ν_{max} 3293, 2979, 2940, 2882, 2358, 2125, 1756, 1515, 1465, 1396, 1373, 1342, 1302, 1275, 1177, 1094, 1062, 1007, 948, 939, 893, 857, 7901, 670.

Crystallographic Studies. Crystallographic studies were undertaken on single crystals mounted inParatone and studied on an Agilent SuperNova Dual three-circle diffractometer using Cu Kα or Mo Kα radiation and a CCD detector. Measurements were typically made at 150(1) K with temperatures maintained using an Oxford Cryostream. Data were collected, integrated, and corrected for absorption using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model within CrysAlisPro.[29] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[30] A summary of crystallographic data are available as Supporting Information, and the structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers (1413179−1413189 and 1429175).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00753.

NMR spectra and crystallographic data (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.M.H. is grateful to the Fonds der Chemischen Industrie for a Chemiefonds scholarship and the Studienstiftung des deutschen Volkes. We thank W.R. Grace for the kind donation of $B(C_6F_5)_3$.

DOI: 10.1021/acs.organomet.5b00753
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REFERENCES

(1) Suh, J. H.; Yum, E. K.; Cho, Y. S. *Chem. Pharm. Bull.* **2015**, *63*, 573−578.

(2) Self, C. R.; Barber, W. E.; Machin, P. J.; Osbond, J. M.; Smithen, C. E.; Tong, B. P.; Wickens, J. C.; Bloxham, D. P.; Bradshaw, D. *J. Med. Chem.* **1991**, *34*, 772−777.

(3) (a) Raval, P.; Jain, M.; Goswami, A.; Basu, S.; Gite, A.; Godha, A.; Pingali, H.; Raval, S.; Giri, S.; Suthar, D.; Shah, M.; Patel, P. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 3103−3109. (b) Zahanich, I.; Kondratov, I.; Naumchyk, V.; Kheylik, Y.; Platonov, M.; Zozulya, S.; Krasavin, M. *Bioorg. Med. Chem. Lett.* **2015**, *25*, 3105−3111.

(4) Machrouhi, F.; Ouhamou, N.; Laderoute, K.; Calaoagan, J.; Bukhtiyarova, M.; Ehrlich, P. J.; Klon, A. E. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 6394−6399.

(5) (a) Gissibl, A.; Finn, M. G.; Reiser, O. *Org. Lett.* **2005**, *7*, 2325−2328. (b) Poyatos, M.; Maisse-François, A.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2006**, *25*, 2634−2641. (c) You, Y.; Seo, J.; Kim, S. H.; Kim, K. S.; Ahn, T. K.; Kim, D.; Park, S. Y. *Inorg. Chem.* **2008**, *47*, 1476−1487.

(6) Soares, A. M. S.; Costa, S. P. G.; Gonçalves, M. S. T. *Tetrahedron* **2010**, *66*, 8189−8195.

(7) (a) Milton, M. D.; Inada, Y.; Nishibayashi, Y.; Uemura, S. *Chem. Commun.* **2004**, 2712−2713. (b) Hashmi, A. S. K.; Rudolph, M.; Schymura, S.; Visus, J.; Frey, W. *Eur. J. Org. Chem.* **2006**, *2006*, 4905−4909. (c) Hashmi, A. S. K.; Schuster, A. M.; Rominger, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 8247−8249. (d) Hashmi, A. S. K. *Pure Appl. Chem.* **2010**, *82*, 657−668.

(8) Arcadi, A.; Cacchi, S.; Cascia, L.; Fabrizi, G.; Marinelli, F. *Org. Lett.* **2001**, *3*, 2501−2504.

(9) Harmata, M.; Huang, C. *Synlett* **2008**, *2008*, 1399−1401.

(10) Ilkgul, B.; Gunes, D.; Sirkecioglu, O.; Bicak, N. *Tetrahedron Lett.* **2010**, *51*, 5313−5315.

(11) Saito, A.; Taniguchi, A.; Kambara, Y.; Hanzawa, Y. *Org. Lett.* **2013**, *15*, 2672−2675.

(12) (a) Chen, C.; Voss, T.; Fröhlich, R.; Kehr, G.; Erker, G. *Org. Lett.* **2011**, *13*, 62−65. (b) Kehr, G.; Erker, G. *Chem. Commun.* **2012**, *48*, 1839−1850.

(13) (a) Pernpointner, M.; Hashmi, A. S. K. *J. Chem. Theory Comput.* **2009**, *5*, 2717−2725. (b) Hashmi, A. S. K. *Gold Bull.* **2003**, *36*, 3−9. (c) Brooner, R. E. M.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 11714−11724.

(14) Zhao, X.; Stephan, D. W. *J. Am. Chem. Soc.* **2011**, *133*, 12448−12450.

(15) (a) Hashmi, A. S. K.; Wieteck, M.; Braun, I.; Nösel, P.; Jongbloed, L.; Rudolph, M.; Rominger. *Adv. Synth. Catal.* **2012**, *354*, 555−562. (b) Chen, C.; Harhausen, M.; Liedtke, R.; Bussmann, K.; Fukazawa, A.; Yamaguchi, S.; Petersen, J. L.; Daniliuc, C. G.; Fröhlich, R.; Kehr, G.; Erker, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 5992−5996. For the formation of dibenzopentalenes from diynes by gold catalysis, see: (c) Vilhelmsen, M. H.; Hashmi, A. S. K. *Chem. - Eur. J.* **2014**, *20*, 1901−1908.

(16) Reddy, J. S.; Xu, B.-H.; Mahdi, T.; Fröhlich, R.; Kehr, G.; Stephan, D. W.; Erker, G. *Organometallics* **2012**, *31*, 5638−5649.

(17) Chen, C.; Frohlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2010**, *46*, 3580−3582.

(18) Melen, R. L.; Hansmann, M. M.; Lough, A. J.; Hashmi, A. S. K.; Stephan, D. W. *Chem. - Eur. J.* **2013**, *19*, 11928−11938.

(19) Hansmann, M. M.; Melen, R. L.; Rominger, F.; Hashmi, A. S. K.; Stephan, D. W. *J. Am. Chem. Soc.* **2014**, *136*, 777−782.

(20) Hansmann, M. M.; Melen, R. L.; Rominger, F.; Hashmi, A. S. K.; Stephan, D. W. *Chem. Commun.* **2014**, *50*, 7243−7245.

(21) For the gold-catalyzed conversions of dipropargyl amines, see: Hashmi, A. S. K.; Molinari, L.; Rominger, F.; Oeser, T. *Eur. J. Org. Chem.* **2011**, *2011*, 2256−2264.

(22) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(23) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369−1377.

(24) (a) Istrate, F. M.; Buzas, A. K.; Jurberg, I. D.; Odabachian, Y.; Gagosz, F. *Org. Lett.* **2008**, *10*, 925−928. (b) Chai, D. I.; Hoffmeister, L.; Lautens, M. *Org. Lett.* **2011**, *13*, 106−109. (c) Lu, Z.; Cui, W.; Xia, S.; Bai, Y.; Luo, F.; Zhu, G. *J. Org. Chem.* **2012**, *77*, 9871−9877. (d) For the coordination of the lactone oxygen to $B(C_6F_5)_3$ see also: Hansmann, M. M.; Rominger, F.; Boone, M. P.; Stephan, D. W.; Hashmi, A. S. K. *Organometallics* **2014**, *33*, 4461−4470.

(25) Routier, S.; Saugé, L.; Ayerbe, N.; Coudert, G.; Mérour, J.-Y. *Tetrahedron Lett.* **2002**, *43*, 589−591.

(26) Stafford, J. A.; Brackeen, M. F.; Karanewsky, D. S.; Valvano, N. L. *Tetrahedron Lett.* **1993**, *34*, 7873−7876.

(27) Padiya, K. J.; Gavade, S.; Kardile, B.; Tiwari, M.; Bajare, S.; Mane, M.; Gaware, V.; Varghese, S.; Harel, D.; Kurhade, S. *Org. Lett.* **2012**, *14*, 2814−2817.

(28) Chalasani, D.; Li, J.; Jackson, N. M.; Payne, M.; Lucht, B. L. *J. Power Sources* **2012**, *208*, 67−73.

(29) *CrysAlisPro, Version 1.171.37.33*; Agilent Technologies (release 27-03-2014, CrysAlis171.NET).

(30) Sheldrick, G. M. *SHELXL-2013*; University of Göttingen, Göttingen, Germany, 2013.

DOI: 10.1021/acs.organomet.5b00753
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