ORGANOMETALLICS

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Diverging Pathways in the Activation of Allenes with Lewis Acids and Bases: Addition, 1,2-Carboboration, and Cyclization

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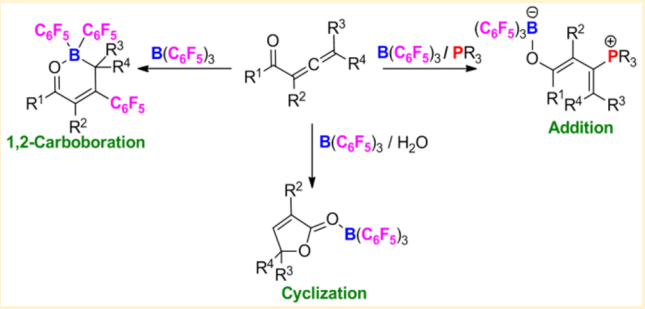
Supporting Information

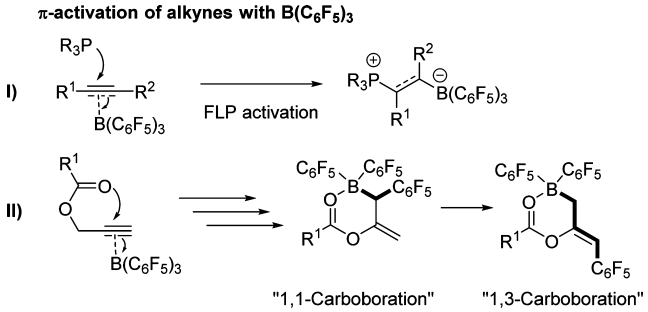
ABSTRACT: The reactions of allenes with frustrated (or cooperative) Lewis acid/base pairs result in the 1,4-addition of the base pair to the allene. The reactions of allenyl ketones and esters just in the presence of the strong Lewis acid $B(C_6F_5)_3$ afford the selective formation of the 1,2-carboboration products. In both cases the Lewis acid activates the allene to either a C_6F_5 migration or nucleophilic attack by the Lewis base. In addition to the 1,2-carboboration pathway, which can be viewed as being triggered by activation of the ketone (σ-activation), in the case of allenyl esters the corresponding cyclization products are observed in the presence of water.



INTRODUCTION

The chemistry of frustrated Lewis pairs (FLPs) has exploded since their first report in 2006.[1] The combination of a Lewis acid and a Lewis base where steric hindrance impedes classical Lewis acid/base adduct formation constitutes an FLP. Owing to the unquenched Lewis acidity and basicity, such systems display unique reactivity and are capable of activating small molecules such as H_2, CO_2, N_2O, SO_2, alkenes, and alkynes, inter alia.[2] In the case of H_2 activation, FLPs have been employed in metal-free hydrogenation catalysis for the reduction of a variety of unsaturated substrates,[2,3] including enantioselective hydrogenations.[4] FLPs have also been shown to effect 1,2-additions to both alkynes and alkenes. In these cases, the Lewis base (e.g., amines, phosphines, thiols, or amides) acts as the nucleophile and the Lewis acid (usually a borane or alane) as the electrophile (Scheme 1, path I).[5] This has also been extended to 1,4-addition processes in the case of 1,3-dienes,[6] 1,3-enynes, and 1,3-diynes.[7] In this context, we have implemented the strong Lewis acid $B(C_6F_5)_3$ to activate the alkyne moiety, thus promoting intramolecular attack by nucleophilic amide or ester functionalities.[8,9] In the case of terminal propargyl esters intramolecular cyclization onto the π-activated alkyne followed by a subsequent C_6F_5 shift from boron to carbon (1,1-carboboration) leads to cyclic allyl boron reagents, which can then undergo a rearrangement reaction to yield the formal 1,3-carboboration products (Scheme 1, path II).[9] While π-Lewis acidic transition metals such as gold can interact strongly with π-bonds,[10] the corresponding boron−π-bond complex has never been isolated, although weak van der Waals interactions have been detected.[11] In FLP chemistry, computational studies have shown that an "encounter complex" forms between the Lewis acid ($B(C_6F_5)_3$), the Lewis base (tBu_3P), and ethylene in which both the Lewis acid and base components of the FLP interact simultaneously with the alkene.[12] In these calculations, the addition reaction was shown to be asynchronous, with the C−B bond forming slightly before P−C bond formation. However, in other cases it was calculated that the borane initially associated with ethylene, which was then followed by 1,2-FLP addition.[13]

Scheme 1. Boron-Mediated π Activation of Alkenes and Alkynes

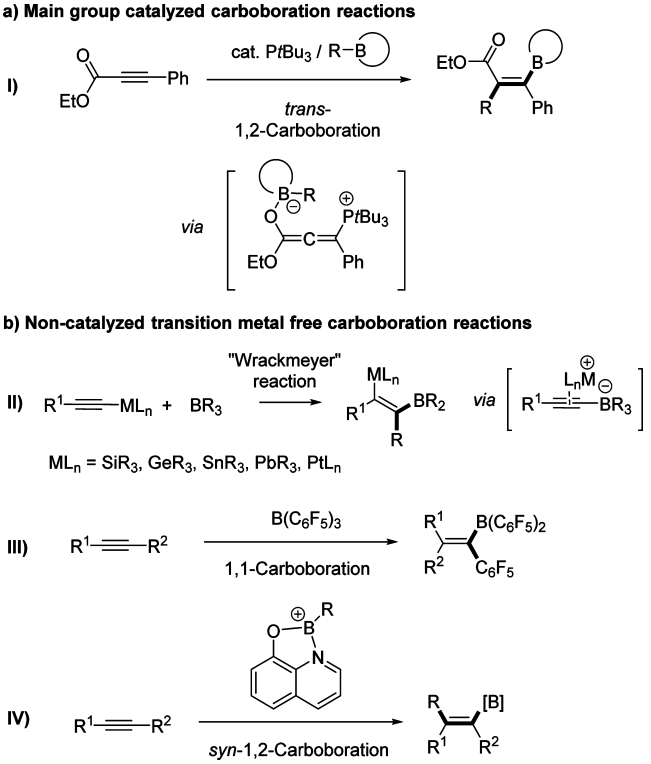


Received: June 23, 2015
Published: August 13, 2015

DOI: 10.1021/acs.organomet.5b00546
Organometallics 2015, 34, 4127−4137

Carboboration reactions of alkynes result in the breaking of the C−B bond in the R_3B starting material and the formation of both R−C and C−BR_2 bonds[14,15] providing a versatile synthetic method to substituted alkenylboranes. Such species have found applications in a variety of organic transformations, including cross-coupling reactions.[16] Typically, transition-metal-based catalysts such as those with copper, palladium, and nickel have been utilized to effect carboboration reactions,[17] although Ohmiya and Sawamura et al. recently reported an elegant approach to afford 1,2-trans-carboboration products using phosphine organocatalysis with alkynoates (Scheme 2, path I).[18] Earlier reports of metal-free, *noncatalyzed*

Scheme 2. Catalyzed and Noncatalyzed Carboboration Reactions



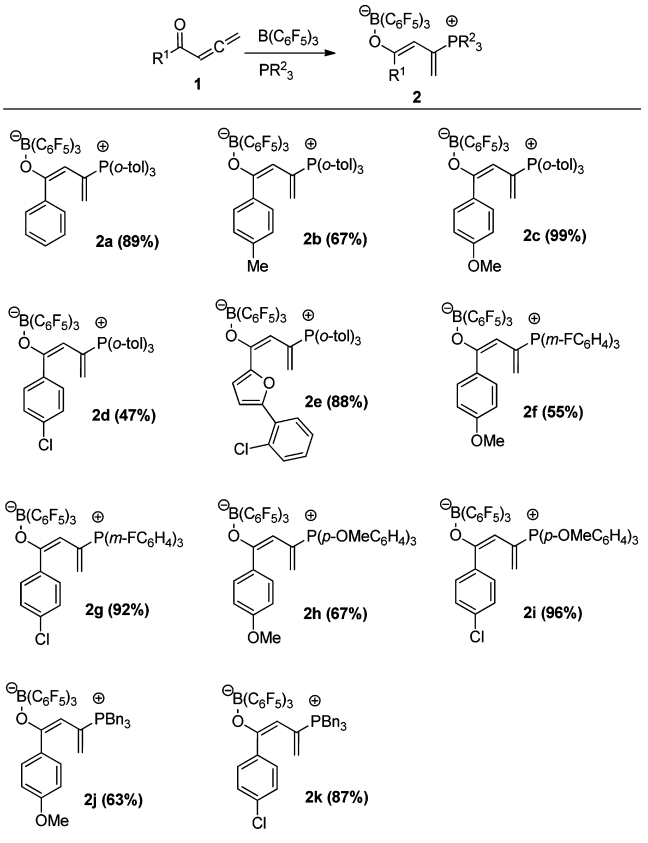
carboboration reactions described as the "Wrackmeyer reaction" involved "activated" alkynes such as acetylides derived from the heavier group 14 elements or terminal metal alkynyl species which reacted in the presence of trialkylboranes.[14,19] In these cases, a 1,2-shift reaction leads to 1,1-carboboration products which are postulated to proceed through the formation of alkynylborates (Scheme 2, path II). In the past few years, the Erker group extended this methodology to "normal" terminal and internal alkynes utilizing the strong Lewis acids $B(C_6F_5)_3$ and $RB(C_6F_5)_2$ to generate alkenylboranes in a 1,1-carboboration reaction (Scheme 2, path III)[14,15] in contrast to 1,2-hydroborations.[20] However, recent work by Ingleson and Bourissou has described borenium systems that effect metal-free syn-1,2-carboborations: for example, in the selective transfer of phenyl and thienyl groups from the borenium system to the alkyne (Scheme 2, path IV).[21]

Herein, we report the reactions of (frustrated) Lewis acid/base pairs with allenes and also show that in the absence of the Lewis base metal-free regioselective 1,2-carboboration reactions of allenes take place using the strong Lewis acid $B(C_6F_5)_3$. Interestingly, Alcarazo et al. studied the FLP-catalyzed hydrogenation of electron-deficient allenes, although the addition reactions of FLPs in the absence of hydrogen were not described.[22]

RESULTS AND DISCUSSION

Reactivity of Allenyl Ketones toward Cooperative Lewis Pairs. We initially investigated the reactions of Lewis acid/base pairs with allenes in the anticipation that the Lewis acid and base could add across the terminal alkene unit of the allene similarly to that observed for the 1,2-addition of FLPs with alkenes and alkynes (Scheme 1, path I).[5] The allene starting materials **1a−e** bearing an electron-withdrawing ketone functionality were synthesized according to standard literature protocols, involving homopropargylation mediated by the in situ generated organozinc compounds followed by Dess−Martin periodinane oxidation (see the Supporting Information). The allenyl ketones **1a−e** were subsequently reacted with the Lewis acid $B(C_6F_5)_3$ and a tertiary phosphine ($P(o\text{-tol})_3$, $P(m\text{-}FC_6H_4)_3$, $P(p\text{-}OMeC_6H_4)_3$, PBn_3) in a 1:1:1 stoichiometric ratio. The in situ NMR-scale reaction of **1a−e** with the Lewis acid/base combination in $CDCl_3$ resulted in an immediate color change to give orange or red solutions in all cases. The reactions were extremely rapid and clean, as observed by NMR (^1H, ^{19}F, ^{11}B, ^{13}C, ^{31}P) spectroscopy, yielding the products **2a−k** (Scheme 3) quantitatively by NMR spectroscopy under ambient conditions, although the isolated yields were sometimes lower. The ^{11}B NMR spectra were all very similar for compounds **2**, displaying a resonance between

Scheme 3. Reactions of Allenyl Ketones 1 with FLPs To Give 2[a]



[a]Isolated yields are indicated.

DOI: 10.1021/acs.organomet.5b00546
Organometallics 2015, 34, 4127−4137

−3.5 and −4.0 ppm. With the exception of **2f,g**, the ^{19}F spectra revealed three signals in a 2:2:1 ratio due to the ortho (δ −132.7 to −133.3 ppm), meta (δ −164.9 to −165.9 ppm), and para (δ −160.1 to −161.2 ppm) fluorine atoms on the pentafluorophenyl rings. For **2f,g**, an additional signal of intensity 1 was also observed at δ −105.5 and −105.2 ppm, respectively, due to the *m*-fluorine atoms on the phosphine. The $^{31}P\{^1H\}$ NMR spectra showed a signal due to the phosphorus environment which was dependent upon the phosphine employed in the reaction: P(*o*-tol)$_3$ (δ 22.8−23.6 ppm (**2b−e**)), P(*m*-FC$_6$H$_5$)$_3$ (δ 22.7−22.8 ppm (**2f,g**)), P(*p*-OMeC$_6$H$_5$)$_3$ (δ 21.7 ppm (**2h,i**)), PBn$_3$ (δ 25.0−25.2 ppm (**2j,k**)).

In the case of **2a−c,f,j,k** crystals could be obtained from the $CDCl_3$ solution. In addition, the stoichiometric reaction of **1b** with B(C$_6$F$_5$)$_3$ and P(*o*-tol)$_3$ on a preparative scale in toluene followed by recrystallization from hexane/toluene yielded a small crop of colorless crystals. Single-crystal X-ray diffraction of the crystals **2a−c,f,j,k** confirmed the identity of these species as the products arising from the addition of the Lewis acid/base pairs to the allene oxygen and β-carbon atom of the allene (Figures 1 and 2).

The metric parameters for **2a−c,f,j,k** are very similar (Table 1). Although the two double bonds C^1=C^2 and C^3=C^4 are conjugated, in the solid state the O−C^1−C^2−C^3-C^4 system is not completely planar with the C^3−C^4 bond twisting out of the O−C^1−C^2 plane, consistent with reduced delocalization of electron density across the π-system. The torsion angles between the C^{1}C^{2}C^3 plane and the C^{2}C^{3}C^4 plane are 29.5(3)° (**2a**), 23.8(5)° (**2b**), 23.8(3)° (**2c**), 14.2(4)° (**2f**), 22.5(3)° (**2j**), and 21.9(2)° (**2k**). This twisting effect presumably arises through crystal packing. Additionally, the aryl ring attached to C^1 also rotates out of the O−C^1−C^2 plane, presumably also a result of steric hindrance. In all cases, it can be seen from the crystal structure that the two alkenes adopt an s-cis configuration.

The Lewis acid/base addition reaction is thought to be initiated by adduct formation between the strong Lewis acid and the ketone oxygen atom through a σ-activation mode. Our previous studies on the reactivity of B(C$_6$F$_5$)$_3$ with related propargyl amides and esters revealed that adduct formation occurred immediately, albeit reversibly, under ambient conditions.[8,9] This O-coordination has the effect of removing electron density from the β-position of the allene, resulting in the buildup of a large partial positive charge at this carbon atom. This renders the β-position susceptible to nucleophilic attack (conjugate addition) from the phosphine resulting in **2a−k** (Scheme 4). The independent reaction of phosphines with the allenes in the absence of B(C$_6$F$_5$)$_3$ showed no reaction, as evidenced by the ^{31}P and $^{31}P\{^1H\}$ NMR spectra, which only show free phosphine. This does not rule out addition of the phosphine to the allene which may be rapid and reversible at room temperature but rather suggests that B(C$_6$F$_5$)$_3$ is necessary for the isolation of the addition product.[23]

Reactivity of Allenyl Ketones and Esters toward B(C$_6$F$_5$)$_3$. The study of the intrinsic reactivity of allene substrates with B(C$_6$F$_5$)$_3$ in the absence of added Lewis base was subsequently investigated. The 1:1 stoichiometric reactions of the allenes **1a−e** with B(C$_6$F$_5$)$_3$ proceeded very rapidly at room temperature (<30 min) to give new compounds in which the B(C$_6$F$_5$)$_3$ underwent a regioselective 1,2-carboboration reaction with the terminal C=C moiety of the allene. Interestingly, Alcarazo et al. observed in the case of electron-rich allenes nucleophilic attack of the central carbon atom onto B(C$_6$F$_5$)$_3$ but did not observe any carboboration due to the enhanced stability of the allene−borane products generated.[22] Products **3a−e** were identified as α,β-unsaturated ketones with a pentafluorophenyl group at the β-position (Scheme 5). The reactions were selective, giving products in which the double-bond configuration is exclusively *E*. The products were fully characterized by multinuclear NMR, mass spectrometry, and/or elemental analysis. In the ^{11}B NMR spectrum a single broad peak observed around 0 ppm is attributed to coordination of the borane to the ketone oxygen atom, yielding an intra-

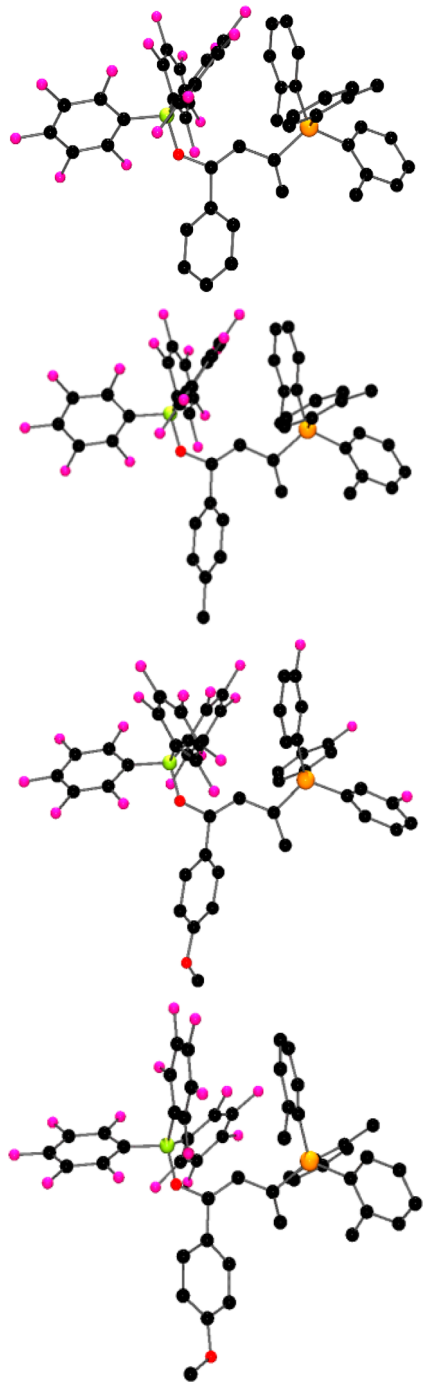


Figure 1. Solid-state molecular structures of **2a−c,f** (from top to bottom): C, black; O, red; B, yellow-green; F, pink; P, orange. Hydrogen atoms are omitted for clarity.

DOI: 10.1021/acs.organomet.5b00546
Organometallics 2015, 34, 4127−4137

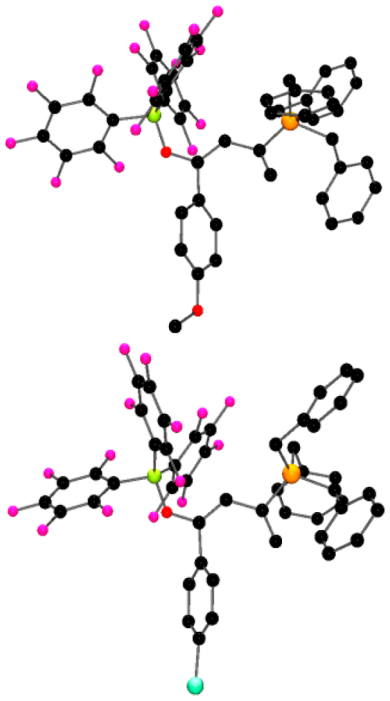


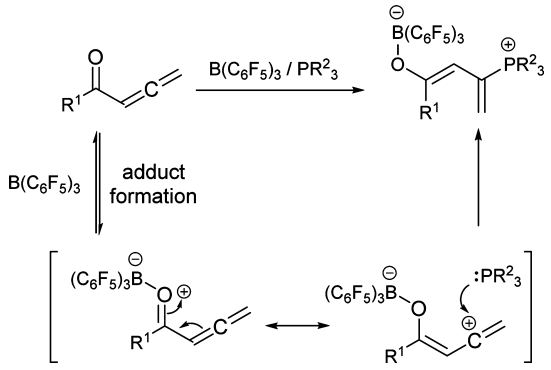
Figure 2. Solid-state molecular structures of **2j,k** (from top to bottom): C, black; O, red; B, yellow-green; F, pink; P, orange; Cl, aquamarine. Hydrogen atoms are omitted for clarity.

molecular chelate analogous to those observed previously for related allyl boron products.[9] In the ^{19}F NMR spectrum six peaks are observed for the two different C_6F_5 rings in a 2:1 ratio.

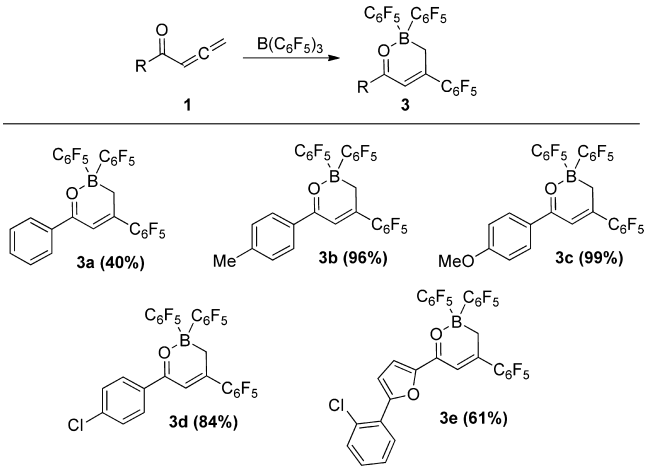
Crystals of **3a,b** suitable for X-ray diffraction could be obtained by dissolving the solid in a few drops of toluene with the addition of 1 drop of hexane and maintaining the temperature at −40 °C. X-ray diffraction analysis confirmed the products as being α,β-unsaturated ketones in which a C_6F_5 group has been transferred to the β-position of the allene and the boron transferred to the γ-position in a net 1,2-carboboration reaction (Figure 3). The structural parameters for the C_4OB heterocycle in the products **3a,b** are the same within error and are included in Table 2.

Further proof of the identity of these compounds was obtained from the reactions of the allenyl esters **4a,b** with $B(C_6F_3)_3$ (Scheme 6). These allenes contain ester functionalities rather than ketones as in the allenes **1** and could be easily prepared in one step in a modified Wittig reaction with the corresponding acyl chlorides (see the Supporting Information).

Scheme 4. Reactions of Allenes with Lewis Acid/Base Pairs



Scheme 5. Reactions of $B(C_6F_5)_3$ with Allenes 1a−e[a]

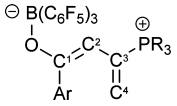


[a]Isolated yields are indicated.

Unlike the reactions of **1** with $B(C_6F_5)_3$, which were rapid at room temperature, the 1:1 reactions of the allenes **4a,b** with $B(C_6F_5)_3$ were inconclusive by in situ NMR in $CDCl_3$. However, the preparative reaction in CH_2Cl_2 showed evidence of the 1,2-carboboration products **5a,b**, respectively, which were formed as a racemic mixture (Scheme 6). Slow evaporation of volatiles from a hexane/CH_2Cl_2 (**5a**) or hexane/toluene (**5b**) solution afforded a very small crop of colorless crystals suitable for single-crystal X-ray diffraction (Figure 4).

In the case of **5a,b**, the structural analysis confirmed that $B(C_6F_5)_3$ had added in a 1,2-fashion across the π-bond of the allene distant from the ester group, with one of the C_6F_5 groups being transferred from boron to carbon. These reactions are

Table 1. Experimental Bond Lengths (Å) in 2a−c,f,j,k



bond	2a	2b	2c	2f	2j	2k
C^1-C^2	1.347(2)	1.352(4)	1.356(2)	1.356(3)	1.359(3)	1.353(2)
C^2-C^3	1.465(3)	1.468(4)	1.464(2)	1.460(3)	1.463(3)	1.466(2)
C^3-C^4	1.337(3)	1.332(5)	1.340(2)	1.339(3)	1.337(3)	1.335(2)
C^1-O	1.339(2)	1.334(4)	1.336(2)	1.337(3)	1.339(2)	1.335(2)
O−B	1.495(3)	1.493(4)	1.489(2)	1.499(3)	1.490(2)	1.493(2)
C^3-P	1.818(2)	1.825(3)	1.811(1)	1.811(2)	1.800(2)	1.804(1)

DOI: 10.1021/acs.organomet.5b00546
Organometallics 2015, 34, 4127−4137

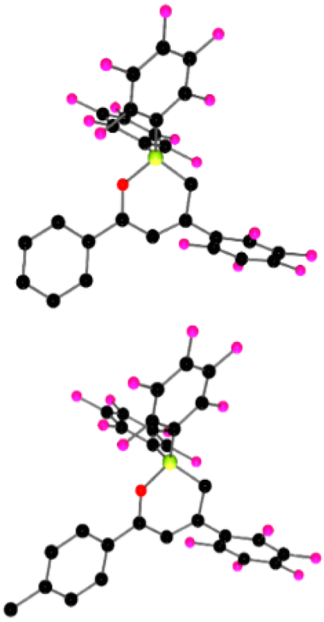
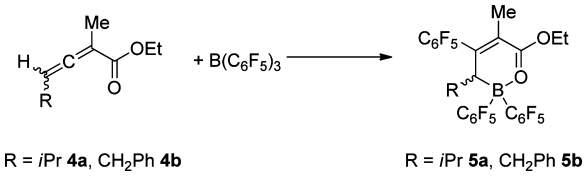


Figure 3. Solid-state molecular structures of **3a** (top) and **3b** (bottom, toluene solvent omitted for clarity): C, black; O, red; B, yellow-green; F, pink. Hydrogen atoms are omitted for clarity.

regioselective, with the C_6F_5 group being transferred to the β-position of the allene and the $B(C_6F_5)_2$ group being installed at the γ-position. The reactions were also selective, giving the *E* isomer, which is presumably a result of the intramolecular nature of the reaction and due to the formation of a stable six-membered chelate product via intramolecular coordination of the ester oxygen to the Lewis-acidic boron center. In both cases the compounds showed a broad peak in the ^{11}B NMR spectrum at 4.2 ppm (**5a**) and 4.5 ppm (**5b**) typical for boron adducts. The structural parameters are summarized in Table 2.

However, the reaction outcome was altered by traces of water in the mixture of allenyl ester **4c** and $B(C_6F_5)_3$. In this case the corresponding γ-lactone cyclization product (**6c**) in which the lactone carbonyl oxygen atom coordinates to $B(C_6F_5)_3$ was obtained in 56% yield (Scheme 7). This compound formulation was verified by single-crystal X-ray diffraction (Figure 5) and resembles compounds typically obtained in catalytic reactions with π-Lewis acidic transition metals such as gold and palladium.[24,25] Further attempts to trigger these cyclization reactions in a catalytic fashion are ongoing but are challenging, as complete suppression of the 1,2-carboboration pathway is required in order to promote lactone formation.

Scheme 6. Reactions of $B(C_6F_5)_3$ with Allenyl Esters 4.



R = *i*Pr **4a**, CH_2Ph **4b** R = *i*Pr **5a**, CH_2Ph **5b**

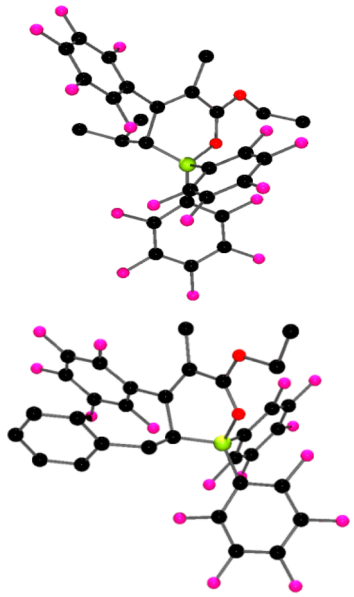


Figure 4. Solid-state molecular structures of **5a** (top, only one of the two independent molecules is shown) and **5b** (bottom): C, black; O, red; B, yellow-green; F, pink. Hydrogen atoms are omitted for clarity.

Scheme 7. Reactions of $B(C_6F_5)_3$ with Allenyl Ester 4c

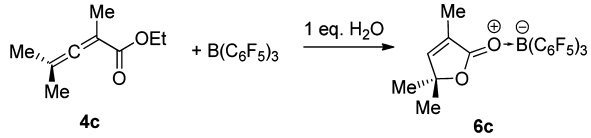
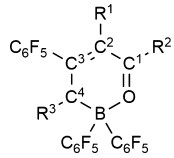


Table 2. Experimental Bond Lengths in 3a,b and 5a,b[a]



			5a		
bond	3a	3b			5b
C^1–C^2	1.437(4)	1.440(3)	1.4661(3)	1.4636(3)	1.4655(16)
C^2–C^3	1.352(3)	1.355(2)	1.3416(3)	1.3482(3)	1.3565(16)
C^3–C^4	1.496(3)	1.497(3)	1.5190(3)	1.5180(3)	1.5235(17)
C^1–O	1.268(3)	1.277(2)	1.2554(2)	1.2557(2)	1.2613(15)
O–B	1.569(3)	1.565(2)	1.5732(3)	1.5723(3)	1.5660(16)
B–C^4	1.604(3)	1.603(3)	1.6183(3)	1.6148(3)	1.6136(17)

[a] **5a** has two molecules in the asymmetric unit.

DOI: 10.1021/acs.organomet.5b00546
Organometallics 2015, 34, 4127–4137

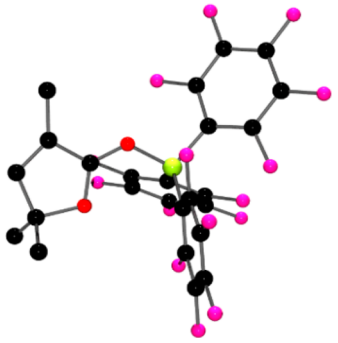
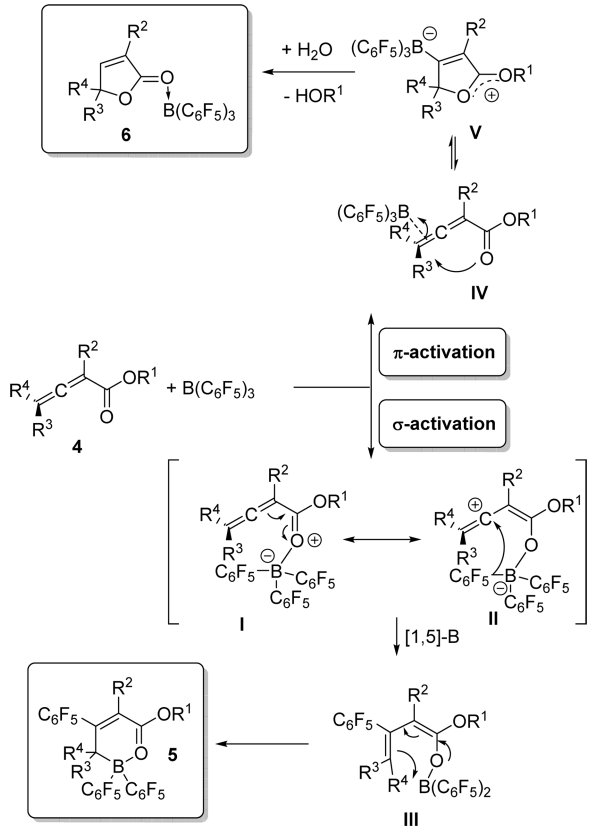


Figure 5. Solid-state structure of compound **6c**: C, black; O, red; B, yellow-green; F, pink. Hydrogen atoms are omitted for clarity.

Mechanistically, we attribute the generation of the 1,2-carboboration and cyclization products to two different potential activation modes: σ-activation (dative bond formation between the carbonyl oxygen atom and boron) and π-activation (Scheme 8). It is possible that a weak van der Waals interaction between the borane and π-bond occurs prior to 1,2-addition, as observed in FLP chemistry,[11] although another possible explanation would be the formation of a covalently bound borate−carbocation intermediate. In the case of alkene−borane π-activation of the allene moiety (**IV**) a vinyl borate compound is formed (**V**). This reactivity is analogous to that observed in transition-metal-catalyzed reactions.[25] Although a pathway involving the $B(C_6F_5)_3$-mediated generation of a strong Brønsted acid (H^+) in the presence of water cannot be excluded, we observe a small sharp peak at δ −15.8 ppm in the in situ ^{11}B NMR spectrum in the 1:1 reaction of allenyl ester **4c** and $B(C_6F_5)_3$. This might be attributed to the generation of the vinyl borate compound **V** (in the cyclization of propargyl amides the corresponding vinyl borate compounds exhibited very similar chemical shifts in the ^{11}B NMR spectra δ ∼−16 ppm).[8,23] In the case where water is present, hydrolysis of **V** takes place releasing the γ-lactone **6** via protodeboronation of the C−B bond and dealkylation of the oxygen atom.[26] The presence of water appears necessary to generate a driving force for the cyclization event, as in its absence conversion to the vinyl borate could not be observed. This suggests a reversible cyclization process, which can only be trapped by the presence of a suitable nucleophile which acts to dealkylate the oxygen atom generating the $B(C_6F_5)_3$-substituted lactone. Subsequent protodeboronation regenerates $B(C_6F_5)_3$ and yields the γ-lactone.

Scheme 8. Proposed Mechanism for σ vs π Activation of Allenyl Esters



The alternative bond activation process leading to the 1,2-carboboration product is triggered by the σ-activation of the carbonyl moiety. Here, adduct formation between the Lewis acid and the ketone oxygen atom reduces the electron density from the β-position of the allene moiety, generating a partial positive charge while at the same time increasing the nucleophilicity of the B−C_6F_5 bond (**I** and **II**). This facilitates migration of the C_6F_5 group to the β-position of the allene, yielding the dienyloxyborane **III** which undergoes a [1,5]-B sigmatropic shift to give the products **3**/**5**. The diastereoselective formation of the double bond in these reactions is presumably due to the formation of a six-membered intramolecular chelate that dictates the geometry of the double bond in the product. This mechanism is also in agreement with the observed selectivity: while the allenyl ketones coordinate more strongly to $B(C_6F_5)_3$ and therefore strongly polarize the allene moiety, the 1,2-carboboration mechanism overpowers other reaction pathways. In contrast, the corresponding allenyl esters form much weaker adducts;[27] therefore, alternative reaction pathways become accessible. In the absence of water 1,2-carboboration products **5** are formed, while in its presence the cyclization pathway yielding **6** can dominate.

Theoretical Considerations. Two sets of representative DFT calculations were undertaken to probe the activity of these acceptor-substituted allenes with respect to (i) addition of a Lewis acid/base pair and (ii) addition of the Lewis acid followed by a subsequent C_6F_5 migration. In the first instance addition of $B(C_6F_5)_3$ to the parent allenyl ketone **1a** was considered followed by addition of triphenylphosphine. In each case the structures were fully optimized at the B3LYP/6-31G* level of theory, followed by thermodynamic calculations based on single-point B3LYP/6-311G*+ computations which were ZPE corrected. Furthermore, a NBO analysis was carried out to probe changes to the bonding scenario. These reveal that σ-coordination of the Lewis acid to the allenyl ketone (Lewis acid/base coordination) is thermodynamically favorable (ΔH = −23 kJ/mol) and leads to an increase in partial charge on the central carbon atom of the allene from +0.12 to +0.21 e. Subsequent addition of PPh_3 is also thermodynamically favorable (ΔH = −55 kJ/mol). The geometric parameters for the final geometry-optimized structure are in good agreement with experimental data. Similarly, studies were undertaken to probe the activation of the allenyl ester MeCH═C═CMeCO$_2$Me (**4d**) by $B(C_6F_5)_3$ followed by C_6F_5 migration. These revealed that initial adduct formation was also favorable by 12 kJ/mol and that C_6F_5-group migration was favored by 111 kJ/mol. Attempts to identify a concerted process in which

DOI: 10.1021/acs.organomet.5b00546
Organometallics 2015, 34, 4127−4137

C_6F_5 migration occurred concomitantly with C−B bond formation proved unsuccessful, suggesting a multistep migration process with one or more transient intermediates. An NBO analysis of the coordination of the Lewis acid to the allenyl ester (**4d**) revealed that while partial charge on the central carbon center of the allene increased upon coordination (from +0.13 to +0.16 e), this increase in partial positive charge was much less pronounced (almost negligible) than that observed with allenyl ketones (see above). This is in accordance with the observations that the allenyl ketones undergo much more rapid C_6F_5-group transfer than the corresponding allenyl esters (see the Supporting Information).

CONCLUSIONS

Addition of a (frustrated) Lewis acid−base pair to acceptor-substituted allenes (allenyl ketones or esters) occurs via O coordination of the ketone to the Lewis acid with the associated activation of the central allene carbon atom toward nucleophilic attack by the phosphine. In the absence of a Lewis base two reaction pathways need to be discriminated: σ-oxygen activation vs π-allene activation. While in the case of the strongly polarized and strongly coordinating allenyl ketones exclusive σ-activation triggers a 1,2-carboboration mechanism, allenyl esters can undergo alternative reaction pathways. In the presence of water the formation of γ-lactone products could be observed, which is reminiscent of reactivity typically effected by π-Lewis acidic transition metals. We should note that the 1,2-carboboration products of the reactions with $B(C_6F_5)_3$ generate organoboron compounds, which might have applications in organic synthesis. Future studies will aim at addressing their reactivity toward organic electrophiles as well as investigating the *catalytic* synthesis of γ-lactones using $B(C_6F_5)_3$.

EXPERIMENTAL SECTION

General Experimental Considerations. With the exception of the synthesis of 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 II 400, Bruker Avance 500, Bruker Avance III 600, and JEOL 300 spectrometers. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CDCl_3$ (7.26/77.16 ppm) and CD_2Cl_2 (5.32/53.80 ppm) as internal standards. 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 the following: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All coupling constants are absolute values, and J values are expressed in hertz (Hz). ^{13}C NMR spectra were all measured as ^{1}H-decoupled. IR spectra were recorded using a Shimadzu IRAffinity-1 spectrophotometer, Elemental analysis was conducted by Mr. Stephen Boyer of London Metropolitan University. Mass spectra were obtained in house using a Waters LCT Premier/XE or a Waters GCT Premier spectrometer and were calculated using ^{10}B. All spectra were analyzed assuming a first-order approximation. For the synthesis of the allene starting materials (**1**) and the reactions of **1** with phosphines along with ^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{31}P, and ^{31}P{^{1}H} NMR spectra for all compounds see the Supporting Information.

Synthesis of 2. *General Procedure.* PR_3 (0.1 mmol, 1 equiv) in $CDCl_3$ (0.5 mL) was added to $B(C_6F_5)_3$ (51 mg, 0.1 mmol, 1 equiv) to give a pale yellow solution, which was then transferred to **1** (0.1 mmol, 1 equiv) to give a red solution. The mixture was transferred to an NMR tube, and the ^{1}H, ^{13}C ^{11}B, ^{19}F, ^{31}P and ^{31}P{^{1}H} NMR spectra were measured. Multinuclear NMR reaction spectra for **2a** were not recorded due to the product precipitating out of solution upon reaction; similarly, an in situ ^{13}C NMR spectrum of **2c** was not recorded for the same reason.

Compound ***2a***. Yield: 58.3 mg, 88.9 μmol, 89%. IR (cm^{-1}): ν_{max} 3054, 2987, 2685, 2412, 2305, 1642, 1558, 1515, 1466, 1423, 1266, 1087, 980, 896, 747, 735, 706. HRMS ESI$^-$: m/z calculated for $[M - H]^-$ $[C_{49}H_{28}BF_{15}OP]^-$, 958.1768; found, 958.1782.

Compound ***2b***. Yield: 65 mg, 66.7 μmol, 67%. Mp: 178−193 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 7.37−7.07 (m, 12H, phosphine C−H), 7.37−7.07 (m, 4H, Ar−H), 5.40 (d, $^3J_{HP}$ = 53 Hz, 1H, C−H), 5.22 (d, $^3J_{HP}$ = 26 Hz, 1H, C−H), 4.34 (d, $^3J_{HP}$ = 11 Hz, 1H, C═CH) 2.45 (s, br, 3H, Ar−CH_3), 2.25 (s, br, 3H, phosphine CH_3), 1.78 (s, br, 3H, phosphine CH_3), 1.59 (s, br, 3H, phosphine CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 165.2 (s), 151.5 (s), 148.9 (s), 146.9 (s), 138.4 (s), 137.5 (s), 134.9 (s), 133.6 (s), 132.2 (s), 130.9 (s), 129.7 (s), 127.7 (s), 93.7 (s), 22.6 (s), 21.5 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −4.0 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −132.7 (m, 2F, *o*-F), −161.1 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-F), −165.9 (m, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 22.9 (s, br). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 298 K): 23.0 (s). IR (cm^{-1}): ν_{max} 3055, 2987, 2925, 2853, 2687, 2412, 2306, 1643, 1586, 1558, 1513, 1465, 1423, 1390, 1373, 1266, 1202, 1137, 1114, 1087, 997, 980, 927, 897, 836, 809, 742, 707. HRMS ESI$^-$: m/z calculated for $[M - H]^-$ $[C_{50}H_{30}BF_{15}OP]^-$, 972.1924; found, 972.1971. Anal. Calcd for $C_{50}H_{31}BF_{15}OP$: C, 61.62; H, 3.21. Found: C, 61.68; H, 3.14.

Compound ***2c***. Yield: 47 mg, 47.4 μmol, 47%. Mp: 176−187 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.28−7.14 (m, 12H, phosphine C−H), 7.52 (d, $^3J_{HH}$ = 8.7 Hz, 2H, *o*-H), 6.89 (d, $^3J_{HH}$ = 8.7 Hz, 2H, *m*-H), 5.54 (d, $^3J_{HP}$ = 52 Hz, 1H, C−H), 5.35 (d, $^3J_{HP}$ = 26 Hz, 1H, C−H), 4.42 (d, $^3J_{HP}$ = 11 Hz, 1H, C═C−H), 3.79 (s, 3H, Ar−OCH_3), 2.45 (s, br, 3H, phosphine CH_3), 1.85 (s, br, 3H, phosphine CH_3), 1.65 (s, br, 3H, phosphine CH_3). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −4.0 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −132.7 (m, 2F, *o*-F), −161.1 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-F), −165.9 (m, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 22.7 (s, br). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 298 K): 22.8 (s). IR (cm^{-1}): ν_{max} 3055, 2988, 2931, 2856, 2687, 2524, 2411, 2306, 1713, 1643, 1610, 1587, 1557, 1513, 1465, 1423, 1390, 1373, 1267, 1175, 1138, 1088, 1032, 980, 925, 908, 897, 842, 808, 756, 724, 706. HRMS ESI$^-$: m/z calculated for $[M - H]^-$ $[C_{50}H_{30}BF_{15}O_2P]^-$, 988.1873; found, 988.1891. Anal. Calcd for $C_{50}H_{31}BF_{15}O_2P{\cdot}CDCl_3$: C, 55.14; H, 2.99. Found: C, 55.07; H, 2.26.

Compound ***2d***. Yield: 98 mg, 98.5 μmol, 99%. Mp: 186−194 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.15−7.17 (m, 12H, phosphine C−H), 7.53 (d, $^3J_{HH}$ = 8.5 Hz, *o*-H), 7.34 (d, $^3J_{HH}$ = 8.5 Hz, *m*-H), 5.52 (d, $^3J_{HP}$ = 52 Hz, 1H, C−H), 5.38 (d, $^3J_{HP}$ = 25 Hz, 1H, C−H), 4.48 (d, $^3J_{HP}$ = 10 Hz, 1H, C−H), 2.44 (s, br, 3H, phosphine CH_3), 1.83 (s, br, 3H, phosphine CH_3), 1.66 (s, br, 3H, phosphine CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 163.8 (m), 149.1 (s), 147.2 (s), 143.9 (s), 143.2 (s), 143.2 (s), 139.0 (s), 137.8 (s), 135.3 (s), 134.7 (s), 134.0 (s), 133.5 (s), 130.0 (s), 129.7 (s), 129.5 (s), 129.3 (s), 126.6 (s), 113.5 (s), 94.6 (m), 26.0 (s), 22.8 (s, br), 21.5 (s), 19.4 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −3.9 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −132.9 (m, 2F, *o*-F), −160.8 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-F), −165.6 (m, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 23.0 (s, br). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 298 K): 23.1 (s). IR (cm^{-1}): ν_{max} 3055, 2987, 2685, 2412, 2308, 1644, 1585, 1556, 1515, 1488, 1466, 1422, 1390, 1371, 1296, 1267, 1202, 1171, 1136, 1122, 1088, 1032, 1016, 996, 979, 926, 910, 898, 844, 808, 750, 729, 706. HRMS ESI$^-$: m/z calculated for $[M - H]^-$ $[C_{49}H_{27}BClF_{15}OP]^-$, 992.1378; found, 992.1411.

Compound ***2e***. Yield: 100 mg, 88.1 μmol, 88%. Mp: 98−115 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 7.59−6.84 (m, 12H, phosphine C−H), 7.59−6.84 (m, 4H, Ar−H), 7.59−6.84 (m, br, 2H, furan C−

DOI: 10.1021/acs.organomet.5b00546
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H), 5.87 (d, $^3J_{HP}$ = 50 Hz, 1H, C−H), 5.63 (d, $^3J_{HP}$ = 23 Hz, 1H, C−H), 4.36 (d, $^3J_{HP}$ = 7.4 Hz, 1H, C═C−H), 2.30 (s, 3H, phosphine CH_3), 1.79 (s, 3H, phosphine CH_3), 1.58 (s, 3H, phosphine CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 151.5 (s), 150.7 (m), 148.3 (s), 147.7 (s), 145.8 (s), 138.6 (s), 136.5 (s), 133.9 (s), 129.8 (s), 128.1 (s), 127.4 (s), 126.8 (s), 125.3 (s), 114.1 (s), 112.2 (s), 95.2 (m), 21.6 (s), 20.0 (m). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −3.6 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −132.9 (m, 2F, *o*-F), −161.2 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-F), −165.7 (m, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 23.7 (s), 19.7 (s, br). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): 23.6 (s), 19.7 (s, br). IR (cm^{-1}): ν_{max} 3055, 2988, 2686, 2522, 2412, 2306, 1712, 1645, 1593, 1566, 1555, 1514, 1466, 1424, 1368, 1265, 1223, 1170, 1137, 1087, 1025, 978, 897, 808, 753, 723, 705. HRMS ESI$^-$: *m*/*z* calculated for $[M - H]^-$ $[C_{53}H_{29}BClF_{15}O_2P]^-$, 1058.1484; found, 1058.1536.

Compound ***2f***. Yield: 55 mg, 54.9 μmol, 55%. Mp: 151−164 °C. ^1H NMR (500 MHz, $CDCl_3$, 298 K): 7.71−7.48 (m, 3H, phosphine C−H), 7.39 (t, br, $^3J_{HH}$ = 8.1 Hz, 3H, phosphine C−H), 7.34 (d, $^3J_{HH}$ = 8.2 Hz, 2H, *o*-H), 7.16 (m, 3H, phosphine C−H), 7.05 (m, 3H, phosphine C−H), 6.74 (d, $^3J_{HH}$ = 8.2 Hz, 2H, *m*-H), 5.63 (d, $^3J_{HP}$ = 53 Hz, 1H, ═C−H), 5.06 (d, $^3J_{HP}$ = 25 Hz, 1H, ═C−H), 4.45 (d, $^3J_{HP}$ = 9.8 Hz, 1H, ═C−H), 3.67 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 166.0 (m), 163.8 (m), 161.9 (m), 160.0 (s), 148.6 (s), 139.6 (s), 137.5 (m), 135.4 (m), 132.9 (s), 132.6 (m), 131.1 (s), 129.7 (s), 129.7 (s), 129.4 (s), 123.1 (m), 120.6 (m), 119.4 (s), 118.8 (s), 114.0 (s), 92.3 (m), 55.1 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −3.8 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −105.5 (m, 1F, phosphine), −133.2 (d, $^3J_{FF}$ = 22 Hz, 2F, *o*-F), 160.8 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-F), 165.6 (t, $^3J_{FF}$ = 21 Hz, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 22.6 (s). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): 22.7 (s). IR (cm^{-1}): ν_{max} 3055, 2987, 2686, 2411, 2306, 1644, 1610, 1585, 1556, 1514, 1480, 1465, 1423, 1270, 1262, 1237, 1175, 1098, 1090, 1033, 999, 981, 925, 897, 844, 794, 757, 723, 706. HRMS AP$^+$: *m*/*z* calculated for $[M]^+$ $[C_{47}H_{22}BF_{18}O_2P]^+$, 1002.1163; found, 1002.1166. Anal. Calcd for $C_{47}H_{22}BF_{18}O_2P$: C, 56.31; H, 2.21. Found: C, 56.27; H, 2.18.

Compound ***2g***. Yield: 93 mg, 92.4 μmol, 92%. Mp: 119−141 °C. ^1H NMR (500 MHz, $CDCl_3$, 298 K): 7.54−7.02 (m, 12H, phosphine C−H) 7.54−7.02 (m, 4H, Ar−H), 5.62 (d, $^3J_{HH}$ = 53 Hz, 1H, ═C−H), 5.11 (d, $^3J_{HH}$ = 25 Hz, 1H, ═C−H), 4.52 (d, $^3J_{HH}$ = 9.4 Hz, 1H, ═CH). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 165.3 (m), 164.4 (m), 162.3 (m), 149.1 (m), 147.2 (m), 140.2 (m), 137.9 (m), 137.7 (s), 135.8 (m), 135.2 (s), 134.2 (m), 133.1 (m), 130.8 (m), 130.0 (m), 129.4 (m), 127.9 (s), 127.3 (s), 123.8 (m), 121.2 (m), 119.7 (m), 119.0 (m), 117.0 (m), 93.6 (m). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −3.8 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −105.2 (m, 1F, P(*m*-FC_6H_4)$_3$), −133.3 (m, 2F, *o*-F), −160.4 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-F), −165.4 (m, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 22.9 (s, br). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): 22.8 (s). IR (cm^{-1}): ν_{max} 3055, 2988, 2964, 2932, 2874, 2861, 2686, 2411, 2307, 1720, 1682, 1644, 1585, 1556, 1514, 1480, 1465, 1424, 1370, 1267, 1235, 1100, 1056, 1015, 998, 979, 966, 926, 898, 843, 794, 752, 731, 707. HRMS ESI$^-$: *m*/*z* calculated for $[M - H]^-$ $[C_{46}H_{18}BClF_{18}OP]^-$, 1004.0626; found, 1004.0672.

Compound ***2h***. Yield: 70 mg, 67.4 μmol, 67%. Mp: 110−122 °C. ^1H NMR (500 MHz, $CDCl_3$, 298 K): 7.32 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar *o*-H), 7.24 (m, 6H, phosphine *m*-H), 6.89 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.5 Hz, 6H, phosphine *o*-H), 6.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H, Ar *m*-H), 5.47 (d, $^3J_{HP}$ = 50 Hz, 1H, ═C−H), 5.00 (d, $^3J_{HP}$ = 24 Hz, 1H, ═C−H), 4.47 (d, $^3J_{HP}$ = 9.0 Hz, 1H, ═CH), 3.77 (s, 9H, phosphine CH_3), 3.66 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 164.8 (s), 164.11 (m), 159.9 (s), 149.0 (s, br), 147.1 (s, br), 137.7 (m), 135.8 (m), 132.0 (s), 131.7 (s), 130.8 (s), 129.9 (s), 115.8 (m), 113.9 (s), 109.2 (s), 108.4 (s), 94.0 (m), 55.7 (s), 55.3 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −3.8 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −133.0 (m, 2F, *o*-F), −161.2 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-F), −165.8 (t, $^3J_{FF}$ = 21 Hz, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 21.8 (s, br). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): 21.7 (s). IR (cm^{-1}): ν_{max} 3055, 2988, 2845, 2687, 2410, 2307, 1713, 1643, 1596, 1568, 1513, 1505, 1464, 1443, 1423, 1364, 1297, 1267, 1184, 1170, 1112, 1084, 1026, 966, 897, 834, 805, 753, 728, 705. HRMS ESI$^-$: *m*/*z* calculated for $[M - H]^-$ $[C_{50}H_{30}BF_{15}O_5P]^-$, 1036.1721; found, 1036.1725.

Compound ***2i***. Yield: 100 mg, 95.9 μmol, 96%. Mp: 87−99 °C. ^1H NMR (500 MHz, $CDCl_3$, 298 K): 7.30 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar *o*-H), 7.24−7.20 (m, 6H, phosphine C−H), 7.12 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar *m*-H), 6.92−6.91 (m, 6H, phosphine C−H), 5.47 (d, $^3J_{HP}$ = 49 Hz, 1H, ═C−H), 5.06 (d, $^3J_{HP}$ = 23 Hz, 1H, ═C−H), 4.54 (d, $^3J_{HP}$ = 8.6 Hz, 1H, ═CH), 3.78 (s, 9H, phosphine CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 164.6 (m), 148.8 (m), 146.7 (m), 136.0 (m), 135.5 (m), 129.8 (s), 129.1 (s), 128.9 (s), 128.5 (s), 128.1 (s), 125.2 (s), 116.6 (m), 115.7 (m), 108.6 (m), 107.9 (m), 55.6 (m), 31.5 (s), 22.6 (s), 21.3 (s), 14.0 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −3.8 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −133.1 (m, 2F, *o*-F), −160.9 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-F), −165.6 (m, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 21.6 (s). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): 21.7 (s). IR (cm^{-1}): ν_{max} 3054, 2988, 2846, 2685, 2309, 1713, 1644, 1594, 1567, 1514, 1504, 1465, 1422, 1366, 1300, 1265, 1223, 1184, 1113, 1088, 1024, 979, 965, 896, 835, 806, 739, 706. HRMS ESI$^-$: *m*/*z* calculated for $[M - H]^-$ $[C_{49}H_{27}BClF_{15}O_4P]^-$, 1040.1225; found, 1040.1245.

Compound ***2j***. Yield: 62 mg, 62.6 μmol, 63%. Mp: 168−181 °C. ^1H NMR (500 MHz, $CDCl_3$, 298 K): 7.39−7.34 (m, 9H, phosphine C−H), 7.39−7.34 (m, 2H, Ar *o*-H) 6.89 (m, 6H, phosphine C−H), 6.80 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar *m*-H), 5.58 (d, $^3J_{HP}$ = 47 Hz, 1H, ═C−H), 5.19 (d, $^3J_{HP}$ = 20 Hz, 1H, ═C−H), 4.87 (d, $^3J_{HP}$ = 8.3 Hz, 1H, ═CH), 3.78 (s, 3H, OCH_3), 3.20 (d, $^3J_{HP}$ = 13 Hz, 6H, phosphine CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 196.9 (s), 164.5 (m), 149.1 (s, br) 147.2 (s, br) 137.9 (s, br), 137.3 (s), 135.9 (m), 134.7 (s), 133.3 (s), 130.3 (m), 129.2 (m), 128.7 (m), 126.1 (s), 91.3 (m), 28.6 (m), 26.0 (m). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −3.57 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −132.9 (m, 2F, *o*-F), −160.3 (t, $^3J_{FF}$ = 21.1, 1F, *p*-F), 165.1 (m, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 25.1 (m). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): 25.0 (s). IR (cm^{-1}): ν_{max} 3055, 2987, 2961, 2926, 2855, 2687, 2411, 2359, 2308, 1716, 1643, 1609, 1588, 1565, 1514, 1498, 1465, 1423, 1365, 1266, 1175, 1088, 1032, 980, 925, 896, 865, 845, 808, 751, 730, 706. HRMS ESI$^-$: *m*/*z* calculated for $[M - H]^-$ $[C_{50}H_{30}BF_{15}O_2P]^-$, 988.1873; found, 988.1896. Anal. Calcd for $C_{50}H_{31}BF_{15}O_2P$: C, 60.63; H, 3.15. Found: C, 60.48; H, 2.94.

Compound ***2k***. Yield: 87 mg, 87.4 μmol, 87%. Mp: 91−103 °C. ^1H NMR (500 MHz, $CDCl_3$, 298 K): 7.29−7.21 (m, 9H, phosphine C−H), 7.29−7.21 (m, 2H, Ar *o*-H), 7.14 (m, 2H, Ar *m*-H), 6.77 (m, 6H, phosphine C−H), 5.42 (d, $^3J_{HP}$ = 47 Hz, 1H, C−H), 5.09 (d, $^3J_{HP}$ = 20 Hz, 1, C−H), 4.8 (d, $^3J_{HP}$ = 8.1 Hz, 1H, ═CH), 3.13 (d, $^3J_{HP}$ = 13 Hz, 6H, phosphine CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 186.7 (s), 167.5 (s), 155.9 (s), 148.3 (s), 139.8 (s), 138.1 (s), 130.3 (m), 129.6 (m), 128.8 (m), 126.2 (s), 93.6 (s), 34.5 (m), 22.4 (m). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): −3.5 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −132.9 (m, 2F, *o*-F), −160.1 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-F), −164.9 (m, 2F, *m*-F). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K): 25.4 (m). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): 25.2 (s). IR (cm^{-1}): ν_{max} 3055, 2987, 2927, 2854, 2687, 2412, 2361, 2307, 1714, 1678, 1645, 1589, 1515, 1464, 1423, 1364, 1266, 1222, 1088, 978, 964, 897, 751, 728, 707. HRMS ESI$^-$: *m*/*z* calculated for $[M - H]^-$ $[C_{49}H_{27}BClF_{15}OP]^-$, 992.1378; found, 992.1357. Anal. Calcd for $C_{49}H_{28}BClF_{15}OP$: C, 59.15; H, 2.84. Found: C, 59.02; H, 2.86.

Alternative Synthesis of 2c. $B(C_6F_5)_3$ (103 mg, 0.2 mmol), P(*o*-tol)$_3$ (60 mg, 0.2 mmol), and 1-(4-methoxyphenyl)buta-2,3-dien-1-one **1c** (36 mg, 0.2 mmol) were mixed in toluene (2 mL), giving a yellow solution. The reaction mixture was left to stand at room temperature for 24 h. Removal of the solvent afforded an orange oil. Washing with hexane (3 × 2 mL) yielded the product **2c** (159 mg, 0.16 mmol, 80%). The addition of hot hexane (ca. 2 mL) and a few drops of hot toluene to give a clear solution gave, upon cooling and prolonged storage (3−4 days), a few colorless needle-shaped crystals of **2c**.

Synthesis of Compounds 3a−e. *General Procedure.* $B(C_6F_5)_3$ (51 mg, 0.1 mmol, 1 equiv) in $CDCl_3$ (0.5 mL) was added to **3** (0.1

DOI: 10.1021/acs.organomet.5b00546
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mmol, 1 equiv), the mixture was transferred to an NMR tube, and the ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were measured.

Compound ***3a***. Yield: 26 mg, 39.6 μmol, 40%. Mp: 48−51 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.26 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, *o*-H), 7.88 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, *p*-H), 7.67 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, *m*-H), 7.33 (s, C−H), 2.74 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 192.6 (s), 169.1 (s), 148.9 (m), 147.0 (m), 146.3 (m), 143.2 (m), 141.4 (m), 141.0 (m), 138.6 (s), 138.3 (m), 137.3 (m), 136.4 (m), 132.9 (s), 131.9 (s), 130.1 (s), 121.2 (s), 116.0 (m), 27.2 (m). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): 2.7 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −135.1 (m, 4F, *o*-F), −138.2 (m, 2F, *o*-F), −149.1 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-F), −157.6 (t, $^{3}J_{FF}$ = 20.7 Hz, 2F, *p*-F), −159.7 (m, 2F, *m*-F), −163.6 (m, 4F, *m*-F). IR (cm^{-1}): ν_{max} 3055, 2988, 2689, 2365, 2307, 1736, 1719, 1651, 1520, 1473, 1422, 1270, 1262, 1096, 982, 897, 759, 721, 708. HRMS ESI^-: *m*/*z* calculated for $[M - H]^-$ $[C_{28}H_7BF_{15}O]^-$: ,654.0387; found, 654.0378.

Compound ***3b***. Yield: 64 mg, 95.5 μmol, 96%. Mp: 48−52 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.19 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, *o*-H), 7.46 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, *m*-H), 7.29 (s, C−H), 2.71 (s, 2H, CH_2), 2.54 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 191.8 (s), 168.1 (s), 151.7 (s), 149.2 (m), 147.4 (s), 145.5 (m), 143.5 (m), 141.3 (m), 138.7 (m), 137.7 (m), 136.7 (m), 132.4 (s), 131.2 (s), 130.6 (s), 121.4 (s), 116.4 (m), 22.8 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): 2.2 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −135.1 (m, 4F, *o*-F), −138.5 (m, 2F, *o*-F), −149.6 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-F), −157.8 (t, $^{3}J_{FF}$ = 20.6 Hz, 2F, *p*-F), −159.9 (m, 2F, *m*-F), −163.7 (m, 4F, *m*-F). IR (cm^{-1}): ν_{max} 3055, 2983, 2686, 2411, 2360, 2343, 2307, 1714, 1650, 1606, 1520, 1486, 1422, 1364, 1319, 1268, 1264, 1223, 1184, 1093, 980, 896, 754, 726, 704. HRMS ESI^-: *m*/*z* calculated for $[M - H]^-$ $[C_{29}H_9BF_{15}O]^-$, 668.0543; found, 668.0535. Anal. Calcd for $C_{29}H_{10}BF_{15}O$: C: 51.97, H: 1.50. Found: C: 51.86, H: 1.46.

Compound ***3c***. Yield: 68 mg, 99.1 μmol, 99%. Mp: 64−71 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.30 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H, *o*-H), 7.23 (s, C−H), 7.11 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H, *m*-H), 4.00 (s, 3H, CH_3), 2.66 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 189.0 (s), 168.8 (s), 165.8 (s), 150.0 (m), 147.0 (m), 145.1 (m), 143.2 (m), 140.7 (m), 138.9 (m), 138.2 (m), 137.2 (m), 136.3 (m), 135.2 (s), 125.5 (s), 120.9 (s), 116.4 (m), 115.8 (s), 56.4 (s), 26.9 (s, br). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): 1.7 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −135.2 (m, 4F, *o*-F), −138.9 (m, 2F, *o*-F), −150.3 (t, $^{3}J_{FF}$ = 20.9 Hz, 1F, *p*-F), −158.2 (t, $^{3}J_{FF}$ = 21.0 Hz, 2F, *p*-F), −160.2 (m, 2F, *m*-F), −163.9 (m, 4F, *m*-F). IR (cm^{-1}): ν_{max} 3056, 2989, 2687, 2413, 2361, 2308, 1713, 1649, 1593, 1572, 1518, 1496, 1465, 1427, 1384, 1271, 1264, 1178, 1095, 1050, 1019, 993, 978, 922, 897, 845, 758, 722, 706. HRMS ESI^-: *m*/*z* calculated for $[M - H]^-$ $[C_{29}H_9BF_{15}O_2]^-$, 684.0605; found, 684.0624.

Compound ***3d***. Yield: 58 mg, 84.0 μmol, 84%. Mp: 61−66 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.22 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, *o*-H), 7.64 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, *m*-H), 7.28 (s, 1H, C−H), 2.75 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 191.4 (s), 170.1 (s), 149.0 (m), 147.0 (m), 146.1 (s), 145.3 (m), 143.3 (m), 141.0 (m), 139.4 (m), 138.4 (m), 137.3 (m), 136.3 (m), 133.0 (s), 131.2 (s), 130.6 (s), 120.8 (s), 115.9 (m), 114.3 (s), 76.2 (s), 27.3 (s), 24.8 (s), 21.1 (m). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): 2.1 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −135.2 (m, 4F, *o*-F), −138.0 (m, 2F, *o*-F), −148.7 (t, $^{3}J_{FF}$ = 21.1 Hz, 1F, *p*-F), −157.4 (t, $^{3}J_{FF}$ = 20.7 Hz, 2F, *p*-F), −159.6 (m, 2F, *m*-F), −163.5 (m, 4F, *m*-F). IR (cm^{-1}): ν_{max} 3055, 2988, 2686, 2362, 2343, 2307, 1712, 1669, 1651, 1520, 1484, 1423, 1363, 1320, 1266, 1223, 1093, 980, 896, 749 732, 706. HRMS ESI^-: *m*/*z* calculated for $[M - H]^-$ $[C_{28}H_6BClF_{15}O]^-$, 687.9997; found, 687.9984.

Compound ***3e***. Yield: 46 mg, 60.8 μmol, 61%. Mp: 58−63 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.04 (s, br, 1H, C−H), 7.81 (m, 1H, C−H), 7.47 (m, 2H, Ar−H), 7.36 (m, 2H, Ar−H), 7.16 (s, 1H, C−H), 2.60 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 176.1 (s, br), 166.5 (s, br), 161.9 (s, br), 149.0 (m), 147.0 (m), 146.2 (m), 143.3 (m), 140.9 (m), 138.4 (m), 136.2 (m), 134.40 (s), 133.0 (s), 132.60 (s), 132.3 (s), 132.11 (s), 131.7 (s), 130.6 (s), 129.8 (s), 127.7 (s, br), 126.6 (s), 120.5 (s), 117.1 (s, br), 116.2 (m), 27.3 (m), 21.4 (s), 20.5 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): 1.9 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −135.1 (m, 4F, *o*-F), −138.3 (m, 2F, *o*-F), −149.9 (t, $^{3}J_{FF}$ = 21 Hz, 1F, *p*-F), −158.1 (t, $^{3}J_{FF}$ = 21 Hz, 2F, *p*-F), −160.1 (m, 2F, *m*-F), −163.9 (m, 4F, *m*-F). IR (cm^{-1}): ν_{max} 3055, 2987, 2686, 2411, 2361, 2343, 2307, 1714, 1651, 1519, 1493, 1482, 1422, 1365, 1320, 1266, 1186, 1093, 1029, 982, 897, 752, 728, 706. Anal. Calcd for $C_{32}H_9BClF_{15}O_2$: C, 50.80; H, 1.20. Found: C, 50.74; H, 1.12.

Synthesis of 5a. $B(C_6F_5)_3$ (103 mg, 0.2 mmol) was dissolved in toluene (1 mL) and was added to ethyl 2,5-dimethylhexa-2,3-dienoate (**4a**; 34 mg, 0.2 mmol) in toluene (1 mL). The reaction mixture was left to stand at room temperature for 24 h, giving an orange solution. Removal of the solvent afforded a dark orange oil. Addition of hexane (2 mL) and a small amount of DCM (ca. 0.5 mL to solubilize the oil) followed by slow evaporation of the solvent afforded colorless crystals of the product. The remaining solution was decanted off and the solid product washed with pentane (3 × 2 mL) and dried in vacuo to give the pure product (36.3 mg, 27%, 0.05 mmol). ^{11}B NMR (128 MHz, $CDCl_3$, 298 K): 4.2 (s, br).

Synthesis of 5b. $B(C_6F_5)_3$ (103 mg, 0.2 mmol) was dissolved in toluene (1 mL) and was added to ethyl 2-methyl-5-phenylpenta-2,3-dienoate (**4b**; 43 mg, 0.2 mmol) in toluene (1 mL), giving a yellow solution upon addition. The reaction mixture was left to stand at room temperature for 24 h. Removal of the solvent afforded a dark orange oil. Addition of hexane (2 mL) and a small amount of toluene (ca. 0.5 mL to solubilize the oil) followed by slow evaporation of the solvent afforded colorless crystals of the product. The remaining solution was decanted off and the solid product washed with pentane (3 × 2 mL) and dried in vacuo to give the pure product (13.7 mg, 9%, 0.02 mmol). ^{1}H NMR (400 MHz, C_6D_6, 298 K): 7.08−7.07 (m, 3H, *o*-H and *p*-H), 6.95 (d, $^{3}J_{HH}$ = 6.6 Hz, 2H, *m*-H), 4.68 and 4.43 (m, 2H, CH_2 diastereotopic), 3.08 and 2.65 (m, 2H, CH_2 diastereotopic), 1.78 (d, $^{4}J_{HH}$ = 2 Hz, 3H, CH_3), 1.51 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, CH_3), 0.88 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H, CH). ^{11}B NMR (128 MHz, C_6D_6, 298 K): 4.5 (s, br). ^{19}F NMR (282 MHz, C_6D_6, 298 K): −132.9 (m, 2F, *o*-F), −133.2 (m, 1F, *o*-F), −137.5 (br s, 2F, *o*-F), −139.3 (m, 1F, *o*-F), −152.2 (t, $^{3}J_{FF}$ = 21 Hz, 1F, *p*-F), −157.2 (t, $^{3}J_{FF}$ = 21 Hz, 1F, *p*-F), −157.8 (t, $^{3}J_{FF}$ = 20 Hz, 1F, *p*-F), −160.4 (m, 1F, *m*-F), −161.5 (m, 1F, *m*-F), −163.3 (m, 2F, *m*-F), −163.6 (m, 2F, *m*-F).

Synthesis of 6. $B(C_6F_5)_3$ (102 mg, 0.2 mmol) was dissolved in toluene (2 mL) and added to ethyl 2,4-dimethylpenta-2,3-dienoate (**4c**; 31 mg, 0.2 mmol) to give a brown solution. After the addition of 1 equiv of H_2O the reaction mixture was left at room temperature for 72 h. Slow evaporation of the solvent gave large brown crystals that were suitable for X-ray diffraction. The remaining solid was washed with hexane (3 × 2 mL) and dried in vacuo to give the pure product (72 mg, 0.12 mmol, 56%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 7.42 (s, 1H, =CH), 2.03 (s, 3H, CH_3), 1.43 (s, 6H, $(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 160.9 (s), 148.8 (s), 146.8 (s), 138.9 (s), 137.8 (s), 135.8 (s), 128.7 (s), 23.7 (s), 17.0 (s), 9.6 (s). ^{11}B NMR (160 MHz, $CDCl_3$, 298 K): 40.4 (s, br), 26.2 (s, br), 1.1 (s, br, B−O adduct), −3.6 (s, br). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K): −134.7 (d, $^{3}J_{FF}$ = 21 Hz, 2F, *o*-F), −157.3 (t, $^{3}J_{FF}$ = 21 Hz, 1F, *p*-F), −164.2 (t, $^{3}J_{FF}$ = 21 Hz, 2F, *m*-F). HRMS ESI^+: *m*/*z* calculated for $[M - B(C_6F_5)_3]^+$ $[C_7H_{10}O_2]^+$, 126.0681; found, 126.0683.

Crystallographic Studies. Crystallographic studies of compounds **2**, **3**, and **6** were undertaken on single crystals mounted in Paratone and studied on an Agilent SuperNova dual four-circle diffractometer using monochromatic Cu Kα (1.54184 Å) or Mo Kα (0.71073 Å) radiation and a CCD detector. Measurements were typically made at 150(1) K with temperatures maintained using an Oxford cryostream. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model within CrysAlisPro.[28] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[29] For compounds **5**, intensity data sets were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer using a sealed X-ray tube and graphite monochromator. Data sets for **5** were corrected for air and detector absorption and Lorentz and polarization

DOI: 10.1021/acs.organomet.5b00546
Organometallics 2015, 34, 4127−4137

effects;[30] absorption by the crystal was treated with a semiempirical multiscan method.[31,32] The structures were solved by direct methods with dual-space recycling[33] (compound **5a**) or by intrinsic phasing[34] (compound **5b**) and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[35] The crystals of **5a** were pseudomerohedrally twinned (twin fractions 0.61:0.39); refinement was against all reflections involving both twin domains. All non-hydrogen atoms were given anisotropic displacement parameters. The positions of most hydrogen atoms (except those of the methyl groups) were taken from difference Fourier syntheses and refined. A summary of crystallographic data are available as Supporting Information, and the structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers 1062326−1062327 and 1062523−1062531).

Computational Studies. DFT calculations were carried out using Jaguar v.8.7.[36] and visualized within Maestro 10.1. All structures were geometry optimized at the B3LYP/6-31G*+ level followed by subsequent thermodynamic single-point energy calculations at the triple-ζ B3LYP/6-311G*+ level and a zero point energy correction made. Determination of partial charges and bond orders were made using the NBO approach.[37]

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge on the ACS publication Web site: The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00546.

Crystallographic data for **2a−c,f,j,k**, **3a,b**, **5a,b**, and **6** (ZIP)

NMR spectra, computational data, and a summary of crystallographic data (PDF)

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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. D.W.S. is grateful for the award of a Canada Research Chair. We thank W. R. Grace for the kind donation of $B(C_6F_5)_3$.

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DOI: 10.1021/acs.organomet.5b00546
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