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Synthesis and Reactivity of Alkynyl-Linked Phosphonium Borates

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Abstract: The phosphine $tBu_2PC\equiv CH$ (**1**) was reacted with $B(C_6F_5)$ to give the zwitterionic species $tBu_2P(H)C\equiv CB(C_6F_5)_3$ (**2**). The analogous species $tBu_2P(Me)C\equiv CB(C_6F_5)_3$ (**3**), $tBu_2P(H)C\equiv CB(Cl)(C_6F_5)_2$ (**4**), $tBu_2P(H)C\equiv CB(H)(C_6F_5)_2$ (**5**), and $tBu_2P(Me)C\equiv CB(H)(C_6F_5)_2$ (**6**) were also prepared. The salt $[tBu_2P(H)C\equiv CB(C_6F_5)_2(THF)][B(C_6F_5)_4]$ (**7**) was prepared through abstraction of hydride by $[Ph_3C][B(C_6F_5)_4]$. Species **5** reacted with the imine $tBuN{=}CHPh$ to give the borane–amine adduct $tBu_2PC\equiv CB[tBuN(H)CH_2Ph](C_6F_5)_2$ (**8**). The related phosphine $Mes_2PC\equiv CH$ (**9**; $Mes = C_6H_2Me_3$) was used to prepare $[tBu_3PH][Mes_2PC\equiv CB(C_6F_5)_3]$ (**10**) and generate $Mes_2PC\equiv CB(C_6F_5)_2$. The adduct $Mes_2PC\equiv CB(NCMe)(C_6F_5)_2$ (**11**) was isolated. Reaction of $Mes_2PC\equiv CB(C_6F_5)_2$ with H_2 gave the zwitterionic product $(C_6F_5)_2(H)BC(H){=}C[P(H)Mes_2]$-$[(C_6F_5)_2BC\equiv CP(H)Mes_2]$ (**12**). Reaction of $tBu_2PC\equiv CB(C_6F_5)_2$, a phosphine–borane generated in situ from **5**, with 1-hexene gave the species $[tBu_2PC\equiv CB(C_6F_5)_2](CH_2CHnBu)$-$[tBu_2PC\equiv CB(C_6F_5)_2]$ (**13**) and subsequent reaction with methanol or hexene resulted in the formation of $[tBu_2P(H)C\equiv CB(C_6F_5)_2]$-$(CH_2CHnBu)[tBu_2PC\equiv CB(C_6F_5)_2]$-$(OMe)$ (**14**) or the macrocycle $\{[tBu_2PC\equiv CB(C_6F_5)_2](CH_2CH_2nBu)\}_2$ (**15**), respectively. In a related fashion, the reaction of **13** with THF afforded the macrocycle $[tBu_2PC\equiv CB(C_6F_5)_2]$-$(CH_2CHnBu)[tBu_2PC\equiv CB(C_6F_5)_2][O$-$(CH_2)_4]$ (**16**), although treatment of $tBu_2PC\equiv CB(C_6F_5)_2$ with THF lead to the formation of $\{[tBu_2PC\equiv CB(C_6F_5)_2][O(CH_2)_4]\}_2$ (**17**). In a related example, the reaction of $Mes_2PC\equiv CB(C_6F_5)_2$ with $PhC\equiv CH$ gave $\{[Mes_2PC\equiv CB$-$(C_6F_5)_2](CH{=}CPh)\}_2$ (**18**). Compound **5** reacted with AlX_3 ($X = Cl$, Br) to give addition to the alkynyl unit, affording $(C_6F_5)_2BC(H){=}C[P(H)tBu_2](AlX_3)$ ($X = Cl$ **19**, Br **20**). In a similar fashion, **5** reacted with $[Zn(C_6F_5)_2]{\cdot}C_7H_8$, $[Al$-$(C_6F_5)_3]{\cdot}C_7H_8$, or $HB(C_6F_5)_2$ to give $(C_6F_5)_3BC(H){=}C[P(H)tBu_2][Zn(C_6F_5)]$ (**21**), $(C_6F_5)_3BC(H){=}C[P(H)tBu_2][Al$-$(C_6F_5)_2]$ (**22**), or $[(C_6F_5)_2B]_2HC{=}CH[P(H)tBu_2]$ (**23**), respectively. The implications of this reactivity are discussed.

Keywords: boranes · borates · frustrated Lewis pairs · phosphanes · phosphonium borates · zwitterions

Introduction

Interest in the chemistry of zwitterionic phosphonium borates garnered particular attention in 2006 with the finding that the species $Mes_2P(H)C_6F_4B(H)(C_6F_5)_2$ ($Mes = C_6H_2Me_3$) reversibly liberates and takes up H_2.[1] This unprecedented heterolytic cleavage of H_2 by a metal-free main-group system was attributed to the cooperative action of unquenched Lewis acidity and basicity on H_2. The inability of these systems to form conventional Lewis acid–base adducts results from steric congestion. Based on this observation, subsequent findings have led to the development of effective metal-free catalysts for the hydrogenation of imines,[2–8] aziridines, and protected nitriles.[2,3] Related alkyl-linked zwitterions, such as $Mes_2P(H)C_2H_4B(H)(C_6F_5)_2$, have also been discovered and shown to catalyze the hydrogenation of enamines,[4,9] silylenol ethers,[6] and selected N heterocycles.[10] In addition, new synthetic routes to such zwitterionic derivatives have been developed from the reactions of sterically encumbered ‘frustrated Lewis pairs’ (FLPs) with a variety of small molecules including olefins,[11–14] alkynes,[15–19] CO_2,[20–22] and N_2O.[23,24] In the case of the reactions of FLPs with alkynes, we have shown that a variety of Lewis bases, including phosphines,[15,17] polyphosphines,[16] amines, thioethers,[18] and pyrroles,[19] will effect addition reactions to give alkenyl-linked zwitterionic products.

In general, alkynyl-linked zwitterions have drawn less attention, although Uhl and co-workers have recently shown that alkynylphosphines react with alanes to give unusual cyclic phosphonium aluminates.[25] To explore the reactivity of alkynyl-linked zwitterionic phosphonium borates, we have recently begun an investigation of the chemistry of the alkynyl zwitterion $tBu_2P(H)C\equiv CB(H)(C_6F_5)_2$. Interestingly, this species reacts with a Ni^0 source with loss of H_2 to generate a Ni–alkyne complex in which B bends towards the Ni, giving rise to an unusual Ni–B interaction (Scheme 1).[26] We have also shown that a related zwitterion undergoes thermal rearrangement to give a unique cumulene derivative, $(tBu_2P)C_6F_4B(F)(C_6F_5)C_4(C_6F_5)_2B(CH_2CHnBu)(PtBu_2)$ (Scheme 1).[27] Herein, we describe an exploration of the generation and reactions of $R_2PC\equiv CB(C_6F_5)_2$ compounds. These “push–pull” alkynyl-linked phosphine boranes are

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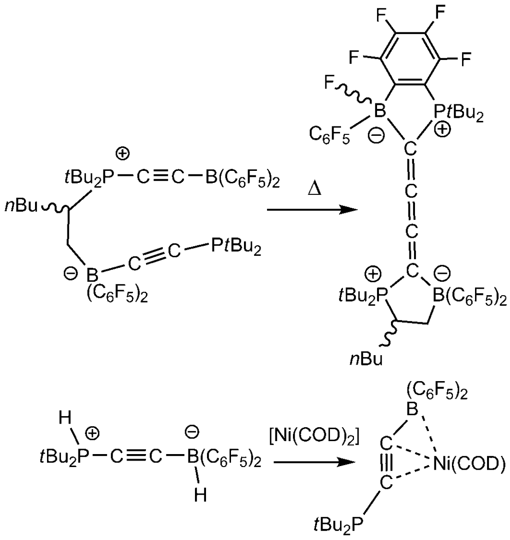


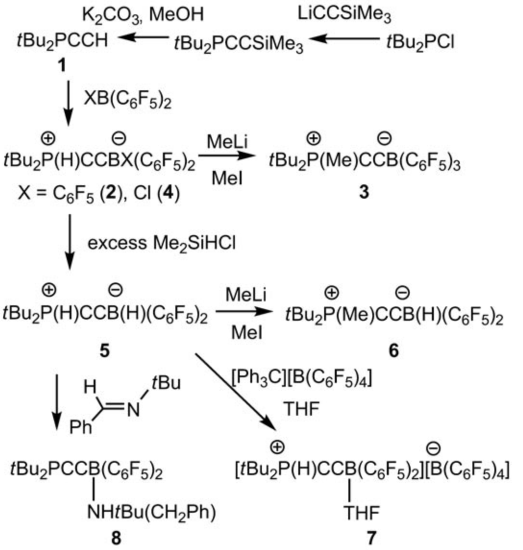
Scheme 1. Reactions of alkynylphosphonium borates. COD = 1,5-cyclooctadiene.

shown to behave as FLPs, affording unique routes to macrocyclic dizwitterions. In addition, $t\mathrm{Bu}_2\mathrm{P(H)C{\equiv}CB(H)(C_6F_5)_2}$ gives interesting Lewis acid addition products. The nature of the products is described and the implications are discussed.

Results and Discussion

Synthesis of alkynylphosphonium borates: The phosphine $t\mathrm{Bu_2PC{\equiv}CH}$ (**1**) was prepared by using a modified literature method[28] and was then reacted with $\mathrm{B(C_6F_5)_3}$ in toluene. The workup gave off-white product **2** in 88 % yield. The ^{1}H and ^{31}P{^{1}H} NMR spectral data for **2** revealed a resonance attributable to a PH fragment and the P chemical shift was consistent with a phosphonium cation. The ^{11}B{^{1}H} NMR chemical shift of **2** at −21.4 ppm was consistent with the presence of a borate fragment. The ^{19}F NMR spectrum of **2** showed resonances consistent with the $\mathrm{C_6F_5}$ rings. These data, together with mass spectrometry data and elemental analyses, support the formula of **2** being the zwitterionic species $t\mathrm{Bu_2P(H)C{\equiv}CB(C_6F_5)_3}$ (Scheme 2). An X-ray crystallographic study of **2** confirmed this formulation (Figure 1 a) with a central C−C bond of 1.217(4) Å and PC≡C and C≡CB angles of 171.2(2) and 174.9(3)°, respectively. Subsequent reaction of **2** with MeLi, followed by treatment with MeI gave **3** in 58 % yield. The ^{31}P{^{1}H} NMR chemical shift at 32.8 ppm and the ^{1}H NMR doublet for $\mathrm{PCH_3}$ at 1.71 ppm are consistent with the structure of **3** being $t\mathrm{Bu_2P(Me)C{\equiv}CB(C_6F_5)_3}$. This was also confirmed crystallographically (Figure 1 b).

In an analogous fashion, the reaction of **1** with $\mathrm{ClB(C_6F_5)_2}$ proceeds easily at −35 °C to give the new off-white product **4** in 72 % isolated yield. Similar to **2**, compound **4** exhibits a ^{1}H NMR doublet resonance at 5.80 ppm, with a P−H coupling constant of 469 Hz, which is indicative of the presence of a PH phosphonium fragment. Compound **4** also exhibits a ^{11}B{^{1}H} NMR signal at −12.8 ppm, consistent with the presence of a borate unit. The ^{31}P{^{1}H} NMR spectrum also gives a signal at 25.5 ppm, shifted downfield from the resonance of the alkynylphosphine (Scheme 2). Collectively these data infer that the formula of **4** is $t\mathrm{Bu_2P(H)C{\equiv}CB(Cl)(C_6F_5)_2}$. This formula was subsequently confirmed by X-ray crystallography, following isolation of suitable crystals from $\mathrm{CH_2Cl_2}$/pentane (Figure 2 a). The metric parameters of **4** were similar to those in **2** and **3**, with a B−Cl bond length of 1.911(4) Å.



Scheme 2. Synthesis of **1**–**8**.

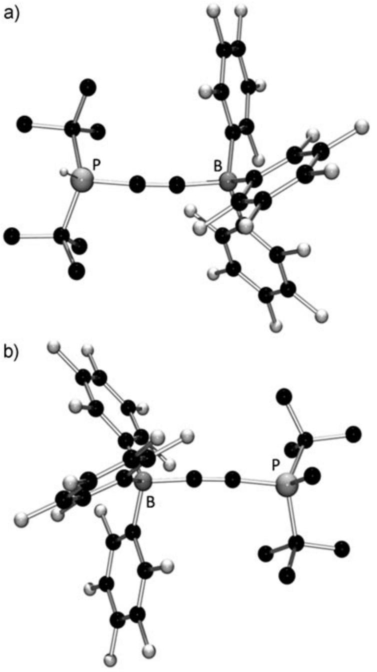


Figure 1. POV-ray depictions of a) **2** and b) **3**.

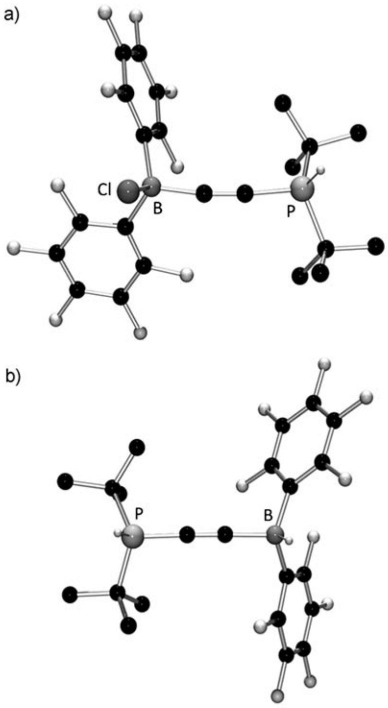


Figure 2. POV-ray depictions of a) **4** and b) **5**.

Treatment of **4** with excess Me_2SiHCl results in exchange of the B-bound chloride for hydride, generating a B−H unit and Me_2SiCl_2. The resulting off-white product **5** was isolated in 79 % yield (Scheme 2). The NMR data confirm the replacement of chloride by hydride, as shown by the observation of a 1:1:1:1 quartet at 3.25 ppm with a B−H coupling constant of 91 Hz, and the $^{11}B\{^1H\}$ NMR resonance shifts to −29.2 ppm. One of the acetylenic carbon atoms is observed in the ^{13}C NMR spectrum at 64.4 ppm with a $^1J_{CP}$ of 158 Hz. The resonance for the B-bound acetylenic carbon was not observed, presumably due to quadrupolar broadening arising from the adjacent B center. Nonetheless, infrared data revealed an absorption at 2125 cm^{-1}, in accord with the presence of the acetylenic unit. The proposed connectivity for **5**, $t Bu_2P(H)C{\equiv}CB(H)(C_6F_5)_2$, was confirmed through X-ray crystallography (Figure 2b), which showed the metric parameters and geometry to be unexceptional. Interestingly, viewing the molecule along the PC≡CB vector in the solid state, it is noted that the substituents on B and P are eclipsed, with the BH and PH groups occupying the same plane.

In a procedure similar to that used to prepare **3**, deprotonation of **5** with MeLi and subsequent treatment with MeI afforded $t Bu_2P(Me)C{\equiv}CB(H)(C_6F_5)_2$ (**6**) in 84 % yield. This formulation is consistent with the ^1H NMR resonances at 1.72 ppm and 3.20 ppm, arising from the P-bound methyl group and the preserved B−H fragment, respectively. In a related reaction of **5**, treatment with $[Ph_3C][B(C_6F_5)_4]$ resulted in the generation of $[t Bu_2P(H)C{\equiv}CB(C_6F_5)_2][B(C_6F_5)_4]$, which was not stable enough to be isolated in pure form. Instead, it was isolated as THF adduct **7** in 77 % yield. The two $^{11}B\{^1H\}$ NMR signals at −3.2 and −16.6 ppm correspond to B bound to THF and the $[B(C_6F_5)_4]$ anion, respectively, inferring abstraction of hydride to form the alkynylphosphonium borate cation. These data, together with other NMR spectra, are consistent with **7** being $[t Bu_2P(H)C{\equiv}CB(C_6F_5)_2\text{-}(THF)][B(C_6F_5)_4]$ (Scheme 2).

Species **5** also reacts with the imine $t BuN{=}CHPh$ in 2 h at 25 °C to give colorless crystals of **8** in 57 % yield. The ^1H NMR data infer the loss of the signals arising from both the PH and BH groups and the generation of new resonances at 5.10 and 3.75 ppm, attributable to the NH and CH_2 groups in the amine $t BuN(H)CH_2Ph$. The $^{31}P\{^1H\}$ NMR resonance at 18.6 ppm suggests a phosphine fragment and the $^{11}B\{^1H\}$ NMR spectrum shows a broad signal at −9.6 ppm. Together with the ^{19}F NMR spectrum, these data infer the formation of the borane–amine adduct $t Bu_2PC{\equiv}CB\text{-}[t BuN(H)CH_2Ph](C_6F_5)_2$ (**8**; Scheme 2). This was subsequently confirmed by an X-ray crystal structure (Figure 3).

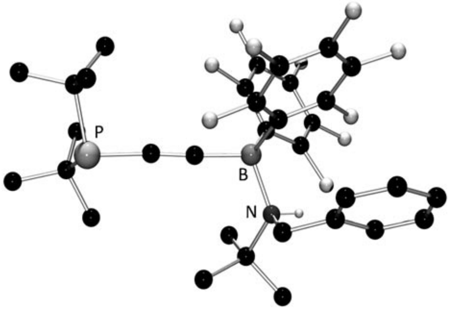
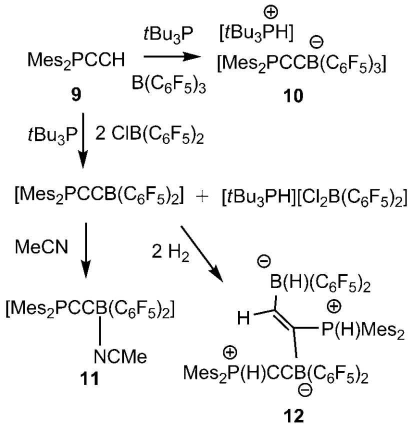


Figure 3. POV-ray depiction of **8**.

The formation of **8** results from proton and hydride transfer to the imine. Although imine reductions have previously been shown to be catalytic with aryl- and alkyl-linked phosphonium borates,[2,29] efforts to utilize **5** as a catalyst to effect the hydrogenation of the imine $t BuN{=}CHPh$ under an H_2 atmosphere at 80 °C were unsuccessful. This was attributed to the inherent reactivity of the polarized alkyne unit in **5**, as these reactions afforded a complex mixture of unidentified degradation products. It is noteworthy that alkynylboranes with strongly electron-withdrawing substituents on B have been reported to be unstable at room temperature and/or in the solid state.[30,31]

To probe the impact of substituent variation, the phosphine $Mes_2PC{\equiv}CH$ (**9**) was prepared by employing a procedure analogous to that used to synthesize **1**. Phosphine **9** was isolated as colorless crystals in 45 % yield. The acetylenic proton gave rise to a ^1H NMR resonance at 2.65 ppm and the $^{31}P\{^1H\}$ NMR resonance was observed at −54.5 ppm. Compound **9** was also characterized crystallographically (see the Supporting Information), confirming the incorporation of the alkynyl fragment. The reaction of **9** with $B(C_6F_5)_3$ and $Pt Bu_3$ gave crystalline product **10** in 87 % yield. This species gave rise to $^{31}P\{^1H\}$ NMR resonances at 61.4 and −52.9 ppm, with a $^{11}B\{^1H\}$ NMR signal at −20.9 ppm, consistent with the presence of a borate unit and supporting the structure of

10 being the salt $[t\mathrm{Bu_3PH}][\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_3}]$. This was unambiguously confirmed crystallographically (Scheme 3, Figure 4). It is noteworthy that the use of $\mathrm{B(C_6F_5)_3}$ and the sterically hindered, yet basic, phosphine $\mathrm{P}t\mathrm{Bu_3}$ to effect deprotonation of the alkyne, affording alkynylborate salts, has been previously shown to be one of the general reactions of FLPs with terminal alkynes.[15]



Scheme 3. Synthesis of **10**–**12**.

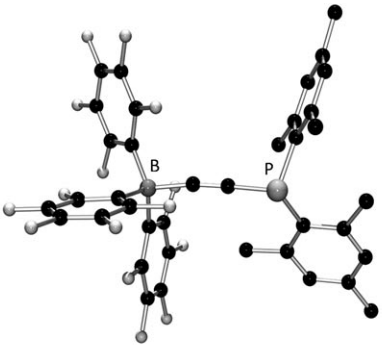


Figure 4. POV-ray depiction of the anion of **10**.

Efforts to form the analogous salt $[t\mathrm{Bu_3PH}][\mathrm{Mes_2PC{\equiv}CBCl(C_6F_5)_2}]$ by employing $\mathrm{ClB(C_6F_5)_2}$ instead of $\mathrm{B(C_6F_5)_3}$ resulted in loss of Cl. This is due to the greater Lewis acidity of $\mathrm{ClB(C_6F_5)_2}$ in comparison with $\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_2}$. Thus, two equivalents of $\mathrm{ClB(C_6F_5)_2}$ were added to a mixture of **9** and $\mathrm{P}t\mathrm{Bu_3}$ to generate $\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_2}$ and $[t\mathrm{Bu_3PH}][\mathrm{Cl_2B(C_6F_5)_2}]$. Subsequent precipitation of the salt byproduct left the alkynylphosphine borane as a red–orange solution. NMR spectra of the solution in $[\mathrm{D_8}]$toluene revealed ^{19}F resonances at −128.9, −147.5, and −162.0 ppm, indicating the presence of a 3-coordinate B centre, as well as giving a $^{31}\mathrm{P}\{^1\mathrm{H}\}$ signal at −53.4 ppm, attributable to the formation of $\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_2}$. However, all efforts to isolate $\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_2}$ were unsuccessful due to the high reactivity of its polarized alkynyl fragment. Nonetheless, addition of acetonitrile allowed the isolation of the yellow adduct $\mathrm{Mes_2PC{\equiv}CB(NCMe)(C_6F_5)_2}$ (**11**) in 53% yield (Scheme 3). The $^{11}\mathrm{B}\{^1\mathrm{H}\}$ NMR signal observed at −12.6 ppm and the ^{19}F NMR signals at −133.9, −157.9, and −164.5 ppm are consistent with the quaternized B center and the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR resonance at −53.0 ppm is consistent with a phosphine fragment. Crystallographic data confirmed this structure (Figure 5) and revealed a B–N bond length of 1.596(2) Å.

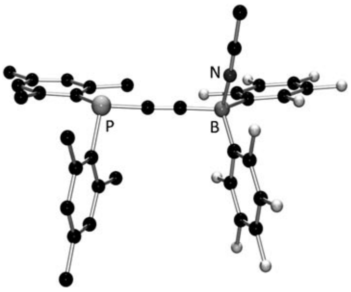


Figure 5. POV-ray depiction of **11**.

Exposure of a solution of the phosphine–borane $\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_2}$, generated in situ from **9**, to $\mathrm{H_2}$ resulted in the isolation of **12** in 37% yield. The ^{1}H and ^{19}F NMR spectra of **12**, obtained at room temperature, contained substantially broadened signals, presumably due to high degrees of rotational inhibition of the bulky substituents. The ^{19}F NMR spectrum measured at 100 °C revealed resonances indicative of two distinct $\mathrm{B(C_6F_5)_2}$ groups. Similarly, the $^{11}\mathrm{B}\{^1\mathrm{H}\}$ NMR data showed signals at −16.9 (a doublet with coupling to P) and −20.3 ppm (broad singlet). Meanwhile, the ^{1}H NMR spectrum obtained at 100 °C showed the presence of an olefinic H coupled to P, two distinct $\mathrm{Mes_2PH}$ groups, and a BH signal. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR resonances also indicated two environments, with signals at −23.3 and −48.7 ppm. The precise nature of **12** was unambiguously determined by crystallography to be $\mathrm{(C_6F_5)_2(H)BC(H){=}C[P(H)Mes_2][(C_6F_5)_2BC{\equiv}CP(H)Mes_2]}$ (Scheme 3, Figure 6). These data reveal that the phosphine–borane activates $\mathrm{H_2}$, although the mechanism for the formation of **12** is unclear. Presumably, the transiently formed $\mathrm{H_2}$ activation species $\mathrm{Mes_2P(H)C{\equiv}CB(H)(C_6F_5)_2}$ reacts with the starting material $\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_2}$ to effect Lewis acid mediated hydride migration from B to the adjacent acetylenic carbon (examples shown later), followed

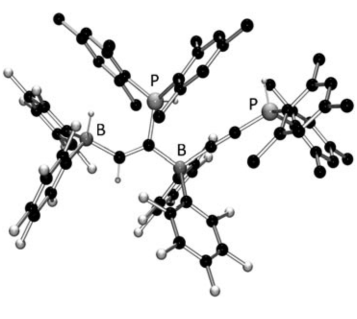


Figure 6. POV-ray depiction of **12**.

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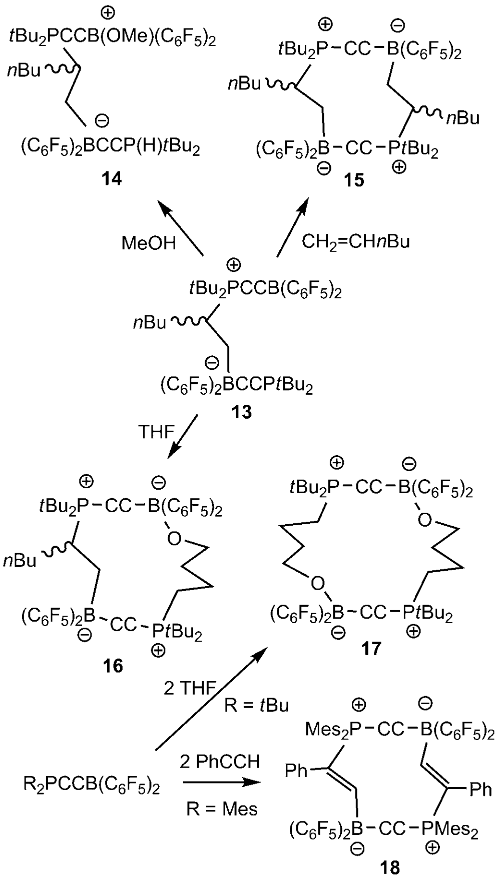
by addition of another H_2 molecule to generate dissymmetric dizwitterion **12**. This reactivity stands in stark contrast to the reversible H_2 activation that allows the facile interconversion of $Mes_2PC_6F_4B(C_6F_5)_2$ and $Mes_2P(H)C_6F_4B(H)(C_6F_5)_2$. Indeed, despite the fact that our alkynyl-linked system demonstrates reactivity typical of an FLP, this reactivity precludes its use as a hydrogenation catalyst.

The corresponding neutral phosphine–borane, $t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2$, was generated in situ through reaction of **5** with $t\mathrm{Bu}_3P$ and $B(C_6F_5)_3$, generating the known salt $[t\mathrm{Bu}_3PH][HB(C_6F_5)_3]$ as a byproduct (Scheme 2). This reaction results from the greater basicity and acidity of $t\mathrm{Bu}_3P$ and $B(C_6F_5)_3$, respectively. Although attempts to isolate the neutral species resulted in unidentified decomposition products, the formation of the phosphine–borane was confirmed by ^{11}B, ^{19}F, and ^{31}P NMR analysis of the reaction mixture. This phosphine–borane generated in situ has previously been found to react with 1-hexene in a ratio of 1:1 to give the species $[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2](n\mathrm{BuCH_2CH})[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2]$ (**13**), which subsequently undergoes thermolysis to give the dissymmetric cumulene $(t\mathrm{Bu}_2P)C_6F_4B(F)(C_6F_5)C_4(C_6F_5)_2B(n\mathrm{BuCH_2CH})(Pt\mathrm{Bu}_2)$.[27] Although **13** could not be structurally characterized, simple treatment of **13** with methanol resulted in the protonation of its free phosphine center with methoxide binding to B, affording $[t\mathrm{Bu}_2P(H)C{\equiv}CB(C_6F_5)_2](n\mathrm{BuCH_2CH})[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2](OMe)$ (**14**) in 74% yield (Scheme 4). This species was crystallized and the structural data confirmed this formulation (Figure 7).

Macrocyclic zwitterionic alkynylphosphonium borates: In probing the reactivity of the above species, we sought to exploit these compounds to form macrocyclic products through FLP reactivity. To that end, an excess of 1-hexene was combined with **13** and heated to 80 °C to form a new species, **15**. Although the formation of the previously reported cumulene derivative was a competing reaction, compound **15** was isolated in 28% yield due to its lower solubility. The $^{11}B\{^1H\}$ NMR spectrum of **15** shows a broad peak at −18.1 ppm and the $^{31}P\{^1H\}$ NMR signals at 43.0 and 41.3 ppm are consistent with the formation of a mixture of diastereomers arising from P/B addition to a second equivalent of olefin. ^1H and ^{19}F NMR data were also in agreement with the generation of two diastereomers. It was speculated that these data are consistent with the dimeric formula $\{[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2](n\mathrm{BuCH_2CH_2})\}_2$ (Scheme 4), a proposition that was confirmed crystallographically (Figure 8). Interestingly, the P/B alkynyl fragment adopts a quasi-parallel geometry. The macrocyclic nature of **15** results in intramolecular P−P and B−B distances of 5.82 and 5.40 Å, respectively.

In other work, we have demonstrated that FLPs are capable of effecting ring-opening reactions of THF,[32] as well as dioxane and thioxane.[33] Herein, we exploit this reactivity to prepare a dissymmetric macrocyclic species through reaction of **13** with THF. This reaction affords the new macrocycle $[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2](n\mathrm{BuCH_2CH})[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2][O(CH_2)_4]$ (**16**) in 81% yield (Scheme 4). The dissymmetry in macrocycle **16** (Figure 9) results in PC≡CB vectors being oriented at an angle of 23.3° with respect to each other. An expanded macrocycle is also accessible through treatment of $t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2$, generated in situ from **5**, with THF alone. This leads to ring opening of THF and the formation of $\{[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2][O(CH_2)_4]\}_2$ (**17**) in 39% isolated yield. Although the spectroscopic data are as expected, the crystallography data (Figure 10) reveals that the symmetry of macrocycle **17** again orients the PC≡CB fragments in an approximately parallel orientation with a dihedral angle of 40.3°, although the intramolecular P−P and B−B distances have lengthened to 6.67 and 7.96 Å, respectively.



Scheme 4. Synthesis of **14**–**18**.

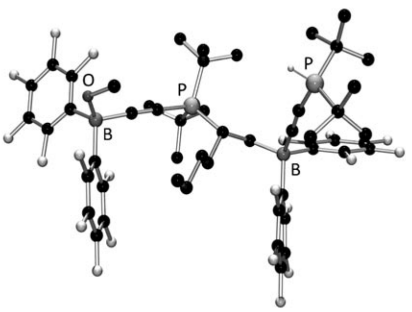


Figure 7. POV-ray depiction of **14**.

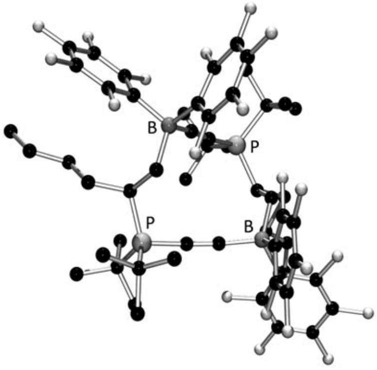


Figure 8. POV-ray depiction of **15**.

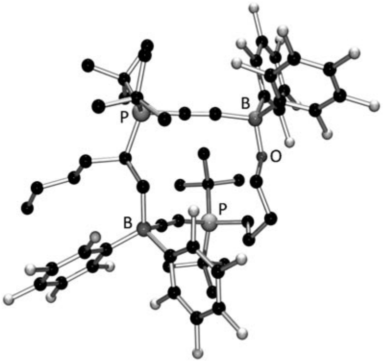


Figure 9. POV-ray depiction of **16**.

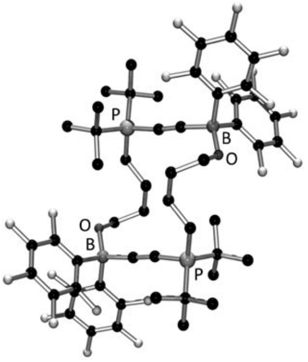


Figure 10. POV-ray depiction of **17**.

In a final example of the use of FLP reactivity to generate macrocycles, the phosphine–borane $Mes_2PC{\equiv}CB(C_6F_5)_2$ was reacted with $PhC{\equiv}CH$. We have previously shown that FLPs that include less basic donors will effect donor and acceptor addition to the alkyne. In the present case, this results in the formation of the macrocyclic product $\{[Mes_2PC{\equiv}CB(C_6F_5)_2](CH{=}CPh)\}_2$ (**18**; Scheme 4, Figure 11). This species is reminiscent of the previously reported macrocyclic species $\{[Mes_2PC_6F_4B(C_6F_5)_2](CH{=}CPh)\}_2$.[18] In **18** the rigidity of the linkages enforces an approximately planar $[PC{\equiv}CBC{=}C]_2$ core, with a maximum deviation from the mean-square plane of 0.181 Å.

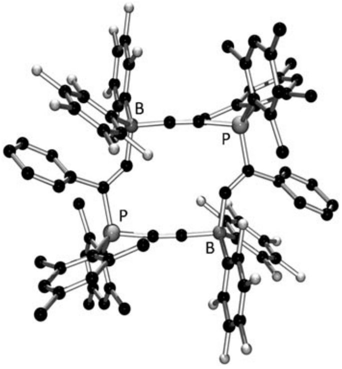
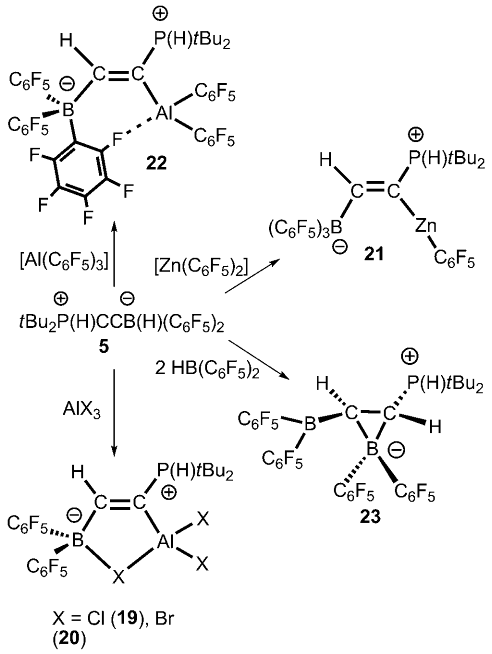


Figure 11. POV-ray depiction of **18**.

Reactions of alkynylphosphonium borates with Lewis acids: In exploring a final aspect of the reactivity of alkynylphosphonium borates, the reactivity with several Lewis acids was probed. Phosphonium borate **5** was reacted with $AlCl_3$ in toluene. After stirring overnight at 25 °C and subsequent workup, a new white solid **19** was isolated in 74 % yield. The $^{31}P\{^1H\}$ NMR spectrum of **19** showed a broad signal at 76.9 ppm and an ^{27}Al resonance was seen at 103.8 ppm. The $^{11}B\{^1H\}$ NMR signal at 12.6 ppm and the ^{19}F NMR resonances at −130.1, −155.3, and −163.9 ppm were all broad, suggesting some fluxional behavior. ^1H NMR data were consistent with the retention of the P–H fragment, as a doublet was observed at 5.42 ppm with a $^1J_{HP}$ of 429 Hz. In addition, a doublet at 8.23 with P–H coupling of 45.9 Hz suggested the reduction of the alkynyl fragment and formation of a =CH fragment. This view was supported by the observation of a $^{13}C\{^1H\}$ NMR signal at 186.9 ppm. In a similar fashion, the corresponding reaction with $AlBr_3$ led to the formation and isolation of **20** in 48 % yield. The NMR data for **20** were similar to those seen for **19**. Both products were structurally characterized by X-ray crystallography to be $(C_6F_5)_2BC(H){=}C[P(H)tBu_2](AlX_3)$ (X = Cl (**19**), Br (**20**); Scheme 5, Figure 12). The two products are similar pseudo-five-membered rings in which the alkynyl fragment is formally reduced to an alkenyl group. Hydride has migrated from boron to the adjacent carbon atom and AlX_3 binds to the carbon atom adjacent to the phosphonium fragment with a halide atom bridge to boron. The Al–C distances in **19** and **20** are 1.958(3) and 1.965(3) Å, respectively, although the resulting C=C bond lengths are identical (1.344(4) Å). The corresponding B–halide distances were found to be 2.198(3) and 2.343(4) Å, respectively. These comparatively large separations are consistent with the fluxional behavior of **19** and **20** in solution. Examination of the dynamic behavior of **19** and **20** by low temperature NMR proved difficult due to their low solubilities.

In a similar fashion, the reaction of **5** with the Lewis acid $[Zn(C_6F_5)_2]{\cdot}C_7H_8$ afforded a new white solid **21** in 70 % yield. This new species exhibited a ^{31}P NMR resonance at 73.6 ppm with P–H coupling of 425 Hz shown in the ^1H NMR spectrum and ^{19}F NMR signals at −130.4, −158.8, and −163.6 ppm. These resonances, together with the



Scheme 5. Synthesis of **19**–**23**.

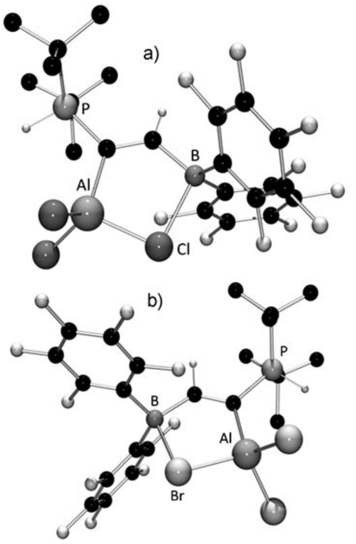


Figure 12. POV-ray depiction of a) **19** and b) **20**.

^{11}B signal at −12.9 ppm are consistent with the presence of a borate fragment derived from B(C_6F_5)$_3$. Additionally, integration of the ^{19}F NMR signals at −117.5, −151.7, and −160.5 ppm are consistent with the presence of an additional C_6F_5 ring, presumably on Zn. Compound **21** also gives rise to ^{1}H signals at 8.92 and 5.28 ppm, attributable to olefinic CH and PH fragments, respectively. These data are consistent with **21** being derived from the combination of the reactants although determining the exact nature of **21** required a crystallographic study. These data unambiguously confirmed the formula of **21** to be (C_6F_5)$_3$BC(H)=C[P(H)*t*Bu$_2$][Zn(C_6F_5)] (Scheme 5, Figure 13), a vinylborate

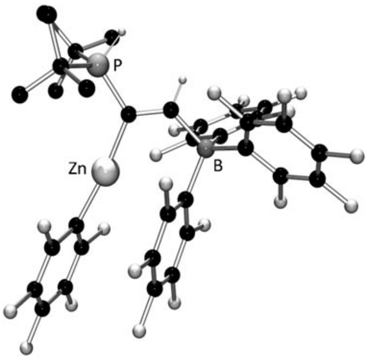


Figure 13. POV-ray depiction of **21**.

derivative. The metric parameters within the borate and phosphonium fragments are as expected. Zn is bound to the olefinic fragment, adopting a linear two-coordinate geometry with a C-Zn-C angle of 172.66(7)° and Zn−C distances to the olefinic and fluoroaryl fragments of 1.928(2) and 1.935(2) Å, respectively.

The analogous reaction of **5** with [Al(C_6F_5)$_3$]•C_7H_8 proceeded in a similarly smooth fashion to give **22** in 61 % yield. The ^{19}F NMR spectrum reveals broad signals that can be attributed to two types of C_6F_5 group which integrate to a 3:2 ratio whereas the sharp ^{11}B resonance at −13.8 ppm is consistent with a 4-coordinate B center. The solid-state structure of **22** was unambiguously confirmed by X-ray crystallography to be (C_6F_5)$_3$BC(H)=C[P(H)*t*Bu$_2$][Al(C_6F_5)$_2$] (**22**; Scheme 5, Figure 14). In this species the Al has added to the C attached to the phosphonium center and the hydride from B has added to the adjacent C atom, resulting in a central olefinic fragment. Interestingly, a C_6F_5 group has migrated to B, affording an anionic B(C_6F_5)$_3$ borate unit. One of the *ortho*-fluorine atoms on the aryl rings on B coordinates to the formally unsaturated Al center with an Al···F of 1.926 Å. A number of reports have described such Al−F interactions.[35,36] It is interesting to note that transfer of a C_6F_5 group normally proceeds from B to Al.[34] However, in **22**, the presence of the phosphonium cation presumably elevates the Lewis acidity of B, as well as the steric congestion around Al.

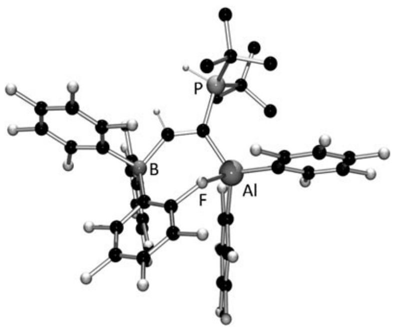


Figure 14. POV-ray depiction of **22**.

Compound **5** also reacts with the Lewis acid $HB(C_6F_5)_2$, yielding a new species **23** in 68% isolated yield. The $^{31}P\{^1H\}$ NMR spectrum of **23** shows a resonance at 55.6 ppm and, along with the ^1H NMR doublet resonance at 4.61 ppm with P−H coupling of 433 Hz, is consistent with retention of the phosphonium fragment. The $^{11}B\{^1H\}$ NMR spectrum of **23** shows two signals, one broad peak at 60.5 ppm and a sharp signal at −15.9 ppm. These peaks infer the presence of three-coordinate borane and four-coordinate borate fragments. The corresponding ^{19}F NMR spectrum showed 18 resonances, suggesting that steric congestion in **23** restricts rotation about the B−C bonds. The ^1H NMR signals at 3.39 and 2.44 ppm can be attributed to methine protons, suggesting full reduction of the alkynyl fragment. The nature of **23** was unambiguously confirmed by X-ray crystallography to be $[(C_6F_5)_2B]_2HC{=}CH[P(H)t\mathrm{Bu}_2]$ (Scheme 5, Figure 15).

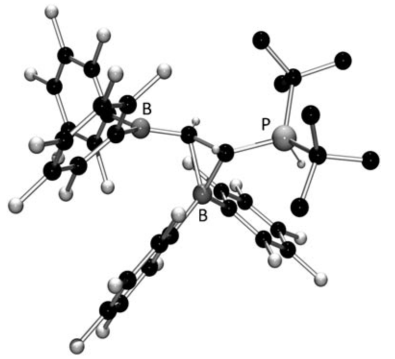


Figure 15. POV-ray depiction of **23**.

This species contains a central boratirane ring, with phosphonium and borane substituents on the C atoms. Within the BC_2 ring, the B_{cyclic}−C(P) and B_{cyclic}−C(B) bonds are 1.609(2) and 1.712(2) Å, respectively, whereas the C−C bond is 1.525(2) Å (average values of the two crystallographically independent molecules in each asymmetric unit). The exocyclic phosphonium and planar borane substituents give rise to P−C and B−C bond lengths to the boratirane ring of 1.774(1) and 1.483(2) Å, respectively. In addition, the B_{cyclic}-C-P and B_{cyclic}-C-B angles are 123.25(11) and 112.18(12)°, respectively. These metric parameters, the large B_{cyclic}−C(B) separation, short exocyclic B−C bond length, and small B_{cyclic}-C-B angle suggest some degree of hyperconjugation in the B_{cyclic}-C-B moiety,[37] which stabilizes the structure of **23**. This reaction is believed to proceed through initial hydroboration of **5** with $HB(C_6F_5)_2$, followed by intramolecular hydride transfer from B to its adjacent C atom, the net effect of which gives the complete reduction of the alkynyl group in **5**.

Conclusion

The results presented herein demonstrate synthetic routes to a variety of alkynylphosphonium borate derivatives. Alkynyl-linked phosphine-boranes react as FLPs in reactions such as the stoichiometric reduction of imines, the addition to olefins and alkynes, and the ring opening of THF. Exploiting this reactivity, synthetic routes to novel macrocyclic products have been developed. In addition alkynylphosphonium borates were shown to react with a variety of Lewis acids, prompting hydride transfer from the borohydride fragment to the alkyne unit, affording reduction to the corresponding olefin. The unique reactivity of related zwitterionic species and the application of FLP reactivity in the synthesis of new materials is still an active area of research in our laboratories.

Experimental Section

General remarks: All manipulations were carried out under an atmosphere of dry, O_2-free N_2 by employing an MBraun glove box and a Schlenk vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass bombs equipped with Young-type Teflon-valve stopcocks (hexanes, pentane, toluene, CH_2Cl_2, THF), or were dried over the appropriate agents and distilled into the same kind of Young bomb (C_6H_5Br, methanol). All solvents were thoroughly degassed after purification (repeated freeze–pump–thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into Young bombs and degassed accordingly (C_6D_5Br, CD_2Cl_2, C_6D_6, $[D_8]$toluene). NMR spectra were recorded at 25°C on Varian 300 and 400 MHz and Bruker 400 MHz spectrometers unless otherwise stated. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal (^1H, ^{13}C) or relative to an external standard (^{11}B: $(Et_2O)BF_3$; ^{19}F: $CFCl_3$; ^{31}P: 85% H_3PO_4). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house by employing a Perkin–Elmer CHN Analyzer. Mes_2PCl,[38] $ClB(C_6F_5)_2$,[39] $[Zn(C_6F_5)_2]{\cdot}C_7H_8$,[40] and $[Al(C_6F_5)_3]{\cdot}C_7H_8$[34] were synthesized according to literature preparations. $[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2](n\mathrm{BuCH_2CH})[t\mathrm{Bu}_2PC{\equiv}CB(C_6F_5)_2]$ (**14**) was prepared as previously reported.[27]

Synthesis of $t\mathrm{Bu}_2PC{\equiv}CH$ (1): This compound was prepared by using a modification of the literature method.

Method 1: A solution of *n*BuLi in hexane (1.6 M, 10.0 mL, 16.0 mmol) was added to a solution of $HC{\equiv}CSiMe_3$ (1.567 g, 15.95 mmol) in THF (20 mL) at 0°C. After stirring at 0°C for 30 min, $ClPt\mathrm{Bu}_2$ (3.00 mL, 15.79 mmol) in THF (15 mL) was added to the reaction mixture at −78°C and stirred at that temperature for 30 min. The reaction was then warmed to room temperature and stirred overnight. THF was evaporated off completely while the flask was kept in an ice bath. The product mixture was redissolved in pentane (15 mL) and filtered through Celite. The solvent was evaporated under vacuum with the flask kept in an ice bath to give $t\mathrm{Bu}_2PC{\equiv}CSiMe_3$. This product was stirred with potassium carbonate (4.42 g. 32.0 mmol) in methanol (17 mL) overnight followed by filtration through Celite. Pentane (10 mL) was then added to the filtrate and the mixture was separated by using a separation funnel under a N_2 atmosphere. The methanol layer was washed twice with pentane (10 mL). The combined pentane phase was passed through a plug of neutral alumina to remove any dissolved methanol. Pentane was evaporated off while the flask was kept in an ice bath. The lightly colored liquid product (1.915 g, 71%) was used in subsequent reactions without further purification. The compound was stored at −35°C to avoid decomposition.

Method 2: The same procedure as above was used for the generation of $t\mathrm{Bu}_2PC{\equiv}CSiMe_3$. This product was then stirred with potassium carbonate in methanol (8 mL) overnight followed by filtration through Celite and washing with pentane (20 mL). The filtrate was then passed through a column of neutral alumina and washed with pentane. Pentane was

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pumped off while the flask was kept in an ice bath to give the product (1.602 g, 56%). ^{1}H NMR (C_6D_6): $\delta=2.55$ (s, 1H; $C\equiv CH$), 1.21 ppm (d, 18H, $^{3}J_{HP}=12.3$ Hz; *t*Bu); ^{13}C{^{1}H} NMR (C_6D_6): $\delta=95.5$ (d, $^{2}J_{CP}=5.0$ Hz; $PC\equiv C$), 84.9 (d, $^{1}J_{CP}=27.9$ Hz; $PC\equiv C$), 33.3 (d, $^{1}J_{CP}=17.4$ Hz; quaternary *t*Bu), 30.6 ppm (d, $^{2}J_{CP}=14.7$ Hz; *t*Bu); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=12.5$ ppm (s); MS (EI): *m/z* calcd: 170.1224; found: 170.1222 [$HC\equiv CPt\mathrm{Bu}_2$]$^{+}$.

Synthesis of *t*Bu$_2$P(H)C≡CB(C$_6$F$_5$)$_3$ (2): A solution of **1** (50 mg, 0.29 mmol) in toluene (3 mL) was added to a solution of $B(C_6F_5)_3$ (150 mg, 0.29 mmol) in toluene (2 mL) at −35 °C. The reaction was stirred at room temperature for 1 h, and toluene was evaporated off. Pentane (10 mL) was then added, and the mixture was filtered and washed with pentane to isolate an off-white product. The product was further dried in vacuo (175 mg, 88%). Single crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a solution of the product in CH_2Cl_2 at 25 °C. ^{1}H NMR (CD_2Cl_2): $\delta=5.71$ (d, 1H, $^{1}J_{HP}=466$ Hz; P*H*), 1.45 ppm (d, 18H, $^{3}J_{HP}=18.8$ Hz; *t*Bu); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-21.4$ ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta=148.7$ (dm, $^{1}J_{CF}=242$ Hz; *o*-C$_6$F$_5$), 139.7 (dm, $^{1}J_{CF}=234$ Hz; *p*-C$_6$F$_5$), 137.3 (dm, $^{1}J_{CF}=240$ Hz; *m*-C$_6$F$_5$), 120.5 (br s; *i*-C$_6$F$_5$), 65.8 (d, $^{1}J_{CP}=173$ Hz; $C\equiv CP$), 35.3 (d, $^{1}J_{CP}=43$ Hz; quaternary *t*Bu), 27.0 ppm (d, $^{2}J_{CP}=2.6$ Hz; *t*Bu), the acetylenic carbon bound to boron was not observed; ^{19}F NMR (CD_2Cl_2): $\delta=-133.1$ (d, 6F, $^{3}J_{FF}=23$ Hz; *o*-C$_6$F$_5$), −161.5 (t, 3F, $^{3}J_{FF}=20$ Hz; *p*-C$_6$F$_5$), −166.6 ppm (m, 6F; *m*-C$_6$F$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=24.5$ ppm (s); MS (EI, CH_2Cl_2): *m/z*: 682.1 [$t\mathrm{Bu}_2P(H)C\equiv CB(C_6F_5)_3$]$^{+}$; elemental analysis calcd (%) for $C_{28}H_{19}BF_{15}P$: C 49.30, H 2.81; found: C 49.36, H 3.02.

Synthesis of *t*Bu$_2$P(Me)C≡CB(C$_6$F$_5$)$_3$ (3): CH_3Li (150 µL, 1.6 M in ether) was added to **2** (163 mL) in toluene (7 mL). The reaction was stirred overnight. The solvents were completely evaporated off and the white solid was washed with pentane. The dry product was redissolved in CH_2Cl_2 (3 mL) and CH_3I (0.5 mL) was then added to the solution.The reaction was stirred overnight and all volatiles were evaporated off. The solid was washed with pentane and recrystallized by layering a CH_2Cl_2 solution of the compound with pentane to give the pure product (96 mg, 58%). Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): $\delta=1.71$ (d, 3H, $^{3}J_{HP}=12.1$ Hz; PC*H$_3$*), 1.39 ppm (d, 18H, $^{3}J_{HP}=16.9$ Hz; *t*Bu); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-21.5$ ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta=148.7$ (dm, $^{1}J_{CF}=237$ Hz; *o*-C$_6$F$_5$), 139.6 (dm, $^{1}J_{CF}=247$ Hz; *p*-C$_6$F$_5$), 137.3 (dm, $^{1}J_{CF}=228$ Hz; *m*-C$_6$F$_5$), 121.1 (br s; quaternary C$_6$F$_5$), 70.5 (d, $^{1}J_{CP}=145$ Hz; $C\equiv CP$), 35.4 (d, $^{1}J_{CP}=47$ Hz; quaternary *t*Bu), 26.7 (d, $^{2}J_{CP}=1.5$ Hz; *t*Bu), 4.4 ppm (d, $^{1}J_{CP}=57$ Hz; PCH$_3$), the $C\equiv CB$ carbon was not observed; ^{19}F NMR (CD_2Cl_2): $\delta=-132.8$ (m, 4F; *o*-C$_6$F$_5$), −161.3 (t, 2F, $^{3}J_{FF}=21$ Hz; *p*-C$_6$F$_5$), −166.3 ppm (m, 4F; *m*-C$_6$F$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=32.8$ ppm (s); elemental analysis calcd (%) for $C_{29}H_{21}BF_{15}P$: C 50.03, H 3.04; found: C 49.49, H 3.08.

Synthesis of *t*Bu$_2$P(H)C≡CB(Cl)(C$_6$F$_5$)$_2$ (4): A solution of **1** (328 mg, 1.93 mmol) in toluene (8 mL) was added to a solution of $ClB(C_6F_5)_2$ (733 mg, 1.93 mmol) in toluene (2 mL) at −35 °C. The reaction was stirred for 1 h, during which time the solution became yellow. After the solvent was completely evaporated off, pentane (12 mL) was added and the mixture was stirred until an off-white solid formed. The supernatant liquid was decanted and the solid product was washed with pentane. Drying in vacuo afforded an off-white powder (761 mg, 72%). This product was used in the subsequent reactions without further purification. Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): $\delta=5.80$ (d, 1H, $^{1}J_{HP}=469$ Hz; P*H*), 1.51 ppm (d, 18H, $^{3}J_{HP}=18.8$ Hz; *t*Bu); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-12.8$ ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta=148.3$ (dm, $^{1}J_{CF}=243$ Hz; *o*-C$_6$F$_5$), 140.1 (dm, $^{1}J_{CF}=251$ Hz; *p*-C$_6$F$_5$), 137.6 (dm, $^{1}J_{CF}=248$ Hz; *m*-C$_6$F$_5$), 119.8 (br s; quaternary C$_6$F$_5$), 67.4 (d, $^{1}J_{CP}=155$ Hz; $C\equiv CP$), 35.4 (d, $^{1}J_{CP}=42$ Hz; quaternary *t*Bu), 27.0 ppm (d, $^{2}J_{CP}=2.5$ Hz; *t*Bu), the $C\equiv CB$ carbon was not observed; ^{19}F NMR (CD_2Cl_2): $\delta=-133.1$ (m, 4F; *o*-C$_6$F$_5$), −160.5 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C$_6$F$_5$), −166.1 ppm (m, 4F; *m*-C$_6$F$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=25.5$ ppm (s); elemental analysis calcd (%) for $C_{22}H_{19}BClF_{10}P$: C 47.99, H 3.48; found: C 47.87, H 3.80.

Synthesis of *t*Bu$_2$P(H)C≡CB(H)(C$_6$F$_5$)$_2$ (5): Compound **4** (368 mg, 0.668 mmol) was stirred with Me_2SiHCl (1.0 g, 5.83 mmol) overnight in CH_2Cl_2 (8 mL). After confirming full conversion to the product by NMR spectroscopy of the reaction mixture, all volatiles were completely removed. The residue was dissolved in toluene (10 mL) and passed through neutral alumina to eliminate high molecular weight impurities. The filtrate was dried and the product was recrystallized by layering a solution of the product in CH_2Cl_2 with pentane at 25 °C overnight. The colorless crystals of product were separated from the supernatant, from which more product was recrystallized by layering a CH_2Cl_2 solution of the compound with pentane. The combined product was dried in vacuo (273 mg, 79%). Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): $\delta=5.70$ (dd, 1H, $^{1}J_{HP}=464$ Hz, $^{5}J_{HH}=2.0$ Hz; P*H*), 3.25 (q, 1H, $^{1}J_{HB}=91$ Hz; B*H*), 1.48 ppm (d, 18H, $^{3}J_{HP}=18.8$ Hz; *t*Bu); ^{11}B{^{1}H} NMR: $\delta=-29.2$ ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta=148.0$ (dm, $^{1}J_{CF}=235$ Hz; *o*-C$_6$F$_5$), 138.8 (dm, $^{1}J_{CF}=245$ Hz; *p*-C$_6$F$_5$), 136.9 (dm, $^{1}J_{CF}=261$ Hz; *m*-C$_6$F$_5$), 120.9 (br s; quaternary C$_6$F$_5$), 64.4 (d, $^{1}J_{CP}=158$ Hz; $C\equiv CP$), 34.7 (d, $^{1}J_{CP}=44$ Hz; quaternary *t*Bu), 26.7 ppm (d, $^{2}J_{CP}=2.6$ Hz; *t*Bu), the $C\equiv CB$ carbon was not observed; ^{19}F NMR (CD_2Cl_2): $\delta=-133.2$ (dm, 4F, $^{3}J_{FF}=21$ Hz; *o*-C$_6$F$_5$), −162.8 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C$_6$F$_5$), −166.7 ppm (m, 4F; *m*-C$_6$F$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=24.2$ ppm (s); IR (CH_2Cl_2): $\tilde{\nu}=2125$ cm^{-1} ($C\equiv C$); elemental analysis calcd (%) for $C_{22}H_{20}BF_{10}P$: C 51.19, H 3.91; found: C 51.35, H 4.02.

Synthesis of *t*Bu$_2$P(Me)C≡CB(H)(C$_6$F$_5$)$_2$ (6): This compound (43 mg, 84%) was prepared in a fashion analogous to **3**. Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): $\delta=3.20$ (q, 1H, $^{1}J_{HB}=91$ Hz; B*H*), 1.72 (d, 3H, $^{2}J_{HP}=12.1$ Hz; PC*H$_3$*), 1.42 ppm (d, 18H, $^{3}J_{HP}=16.9$ Hz; *t*Bu); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-29.2$ ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta=148.4$ (dm, $^{1}J_{CF}=238$ Hz; *o*-C$_6$F$_5$), 139.1 (dm, $^{1}J_{CF}=239$ Hz; *p*-C$_6$F$_5$), 137.3 (dm, $^{1}J_{CF}=246$ Hz; *m*-C$_6$F$_5$), 121.7 (br s, quaternary C$_6$F$_5$), 69.4 (d, $^{1}J_{CP}=165$ Hz; $C\equiv CP$), 35.3 (d, $^{1}J_{CP}=48$ Hz; quaternary *t*Bu), 26.8 (d, $^{2}J_{CP}=1.3$ Hz; *t*Bu), 4.7 ppm (d, $^{1}J_{CP}=57$ Hz; C*H$_3$*), the $C\equiv CB$ carbon was not observed; ^{19}F NMR (CD_2Cl_2): $\delta=-132.9$ (d, 4F, $^{3}J_{FF}=20$ Hz; *o*-C$_6$F$_5$), −162.7 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C$_6$F$_5$), −166.4 ppm (m, 4F; *m*-C$_6$F$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2): 31.9 ppm (s); elemental analysis calcd (%) for $C_{23}H_{22}BF_{10}P$: C 52.10, H 4.18; found: C 51.74, H 3.97.

Synthesis of [*t*Bu$_2$P(H)C≡CB(C$_6$F$_5$)$_2$(THF)][B(C$_6$F$_5$)$_4$] (7): A solution of **5** (50 mg, 0.097 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a stirring solution of [CPh$_3$][B(C$_6$F$_5$)$_4$] (66 mg, 0.072 mmol) in CH_2Cl_2 (1 mL) until the intense yellow color of [CPh$_3$][B(C$_6$F$_5$)$_4$] faded (not all of the solution of **5** was used). The reaction mixture was stirred for a further 5 min, followed by addition of THF (30 µL, 0.37 mmol) and stirring for another 5 min. The colorless solution was evaporated down to ≈0.5 mL. Addition of pentane (5 mL) precipitated a sticky solid product, which was left to stir for 3 h. The mother liquor was removed and the sticky solid dried in vacuo. The product was further recrystallized by layering a CH_2Cl_2 solution of the compound with pentane at RT (70 mg, 77%). ^{1}H NMR (CD_2Cl_2): $\delta=5.83$ (d, 1H, $^{1}J_{HP}=475$ Hz; P*H*), 4.37 (m, 4H; O(C*H$_2$*CH$_2$)$_2$), 2.30 (m, 4H; O(CH$_2$C*H$_2$*)$_2$), 1.51 ppm (d, 18H, $^{3}J_{HP}=19.2$ Hz; *t*Bu); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-3.2$ (br s; *B*(THF)), −16.6 ppm (s; *B*(C$_6$F$_5$)$_4$); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta=150.3$–135.5 (overlapping broad signals for *o*-, *p*-, and *m*-C$_6$F$_5$), 124.6 (br s; *i*-C$_6$F$_5$, B(C$_6$F$_5$)$_4$), 113.2 (br s, *i*-C$_6$F$_5$, B(C$_6$F$_5$)$_2$), 78.1 (s; O(*C*H$_2$CH$_2$)$_2$), 73.7 (d, $^{1}J_{CP}=143$ Hz; $C\equiv CP$), 35.7 (d, $^{1}J_{CP}=39$ Hz; quaternary *t*Bu), 27.0 (d, $^{2}J_{CP}=3.0$ Hz; *t*Bu), 25.7 ppm (s; O(CH$_2$*C*H$_2$)$_2$), the $C\equiv CB$ was not observed; ^{13}C{^{19}F} NMR (CD_2Cl_2): $\delta=147.2$ (s; *o*-C$_6$F$_5$, B(C$_6$F$_5$)$_4$), 146.7 (s; *o*-C$_6$F$_5$, B(C$_6$F$_5$)$_2$), 140.5 (s; *p*-C$_6$F$_5$, B(C$_6$F$_5$)$_2$), 137.4 (s; *p*-C$_6$F$_5$, B(C$_6$F$_5$)$_4$), 136.9 (s; *m*-C$_6$F$_5$, B(C$_6$F$_5$)$_2$), 135.5 (q, $^{3}J_{CB}=3.0$ Hz; *m*-C$_6$F$_5$, B(C$_6$F$_5$)$_4$), 123.4 ppm (q, $^{1}J_{CB}=51$ Hz; *i*-C$_6$F$_5$, B(C$_6$F$_5$)$_4$); ^{19}F NMR (CD_2Cl_2): $\delta=-133.5$ (m, 8F; *o*-C$_6$F$_5$, B(C$_6$F$_5$)$_4$), −133.8 (m, 4F; *o*-C$_6$F$_5$, B(C$_6$F$_5$)$_2$), −153.9 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C$_6$F$_5$, B(C$_6$F$_5$)$_2$), −162.4 (m, 4F; *m*-C$_6$F$_5$, B(C$_6$F$_5$)$_2$), −164.1 (t, 4F, $^{3}J_{FF}=20$ Hz; *p*-C$_6$F$_5$, B(C$_6$F$_5$)$_4$), −168.0 ppm (m, 8F; *m*-C$_6$F$_5$, B(C$_6$F$_5$)$_4$); ^{31}P{^{1}H} NMR (CD_2Cl_2): 26.8 ppm (s); elemental analysis calcd (%) for $C_{50}H_{27}B_2F_{30}OP$: C 47.43, H 2.15; found: C 47.83, H 2.58.

Synthesis of $t\mathrm{Bu_2PC{\equiv}CB}[t\mathrm{BuN(H)CH_2Ph}](\mathrm{C_6F_5})_2$ (8): Compound **5** (32 mg, 0.06 mmol) and $t\mathrm{BuN{=}CHPh}$ (10 mg, 0.06 mmol) were stirred in $\mathrm{CH_2Cl_2}$ (1–2 mL) for 2 h at RT. Colorless crystals formed from the concentrate at −35 °C over 2 d. The supernatant liquid was quickly decanted and the crystals were washed with cold pentane and dried. More crystalline product was obtained from the combined and concentrated washings at −35 °C (24 mg, 57 %). The crystalline product was suitable for X-ray diffraction. ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta=6.82$ (m, 3H; Ph), 6.52 (brs, 2H; Ph), 5.10 (brs, 1H; NH), 3.75 (brs, 2H; CH_2), 1.41 (brs, 18H; PtBu$_2$), 1.26 ppm (s, 9H; NtBu); ^{11}B{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta=-9.6$ ppm (brs); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta=148.6$ (dm, $^{1}J_{\mathrm{CF}}=243$ Hz; o-$\mathrm{C_6F_5}$), 140.8 (dm, $^{1}J_{\mathrm{CF}}=243$ Hz; p-$\mathrm{C_6F_5}$), 138.0 (dm, $^{1}J_{\mathrm{CF}}=249$ Hz; m-$\mathrm{C_6F_5}$), 135.9 (s; quaternary Ph), 129.2 (s; Ph), 126.1 (s; Ph), 119.7 (brs; quaternary $\mathrm{C_6F_5}$), 65.3 (brs; $\mathrm{C{\equiv}CP}$), 53.7 (s; quaternary NtBu), 53.3 (s; $\mathrm{CH_2}$), 33.5 (d, $^{1}J_{\mathrm{CP}}=17$ Hz; quaternary PtBu$_2$), 30.5 (d, $^{2}J_{\mathrm{CP}}=14$ Hz; PtBu$_2$), 28.4 ppm (s; NtBu), the $\mathrm{C{\equiv}CB}$ carbon was not observed; ^{19}F NMR ($\mathrm{C_6D_6}$): $\delta=-128.5$ (brs, 2F; o-$\mathrm{C_6F_5}$), −128.9 (brs, 2F; o-$\mathrm{C_6F_5}$), −156.9 (brs, 2F; p-$\mathrm{C_6F_5}$), −163.9 (brs, 2F; m-$\mathrm{C_6F_5}$), −164.2 ppm (brs, 2F; m-$\mathrm{C_6F_5}$); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta=18.6$ ppm (s); elemental analysis calcd (%) for $\mathrm{C_{33}H_{35}BF_{10}NP}$: C 58.43, H 5.20, N 2.21; found: C 58.05, H 5.60, N 2.30.

Synthesis of $\mathrm{Mes_2PC{\equiv}CH}$ (9): The procedure for the synthesis of **1** was followed in general except for the work up. $\mathrm{Me_3SiC{\equiv}CPMes_2}$ was synthesized by using $\mathrm{Me_3SiC{\equiv}CH}$ (1.2 g, 12.2 mmol), nBuLi (1.6 M hexane solution, 6.7 mL, 10.7 mmol), and $\mathrm{Mes_2PCl}$ (3.00 g, 9.84 mmol). After $\mathrm{Mes_2PC{\equiv}CH}$ was formed in methanol with potassium carbonate (3.0 g, 22 mmol), the methanol was completely evaporated from the reaction mixture. The product was extracted with pentane, filtered through Celite, passed through a plug of neutral alumina, and recrystallized from pentane to yield colorless crystals that were further dried in vacuo (1.293 g, 45 %). This crystalline product was suitable for X-ray diffraction. ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta=6.66$ (d, 4H, $^{4}J_{\mathrm{HP}}=2.8$ Hz; Ar-H), 2.65 (s, 1H; $\mathrm{C{\equiv}C}H$), 2.48 (s, 12H; o-CH_3), 2.04 ppm (s, 6H; p-CH_3); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta=142.0$ (d, $^{2}J_{\mathrm{CP}}=16.1$ Hz; 2,6-$\mathrm{C_6H_2}$), 138.3 (s; 4-$\mathrm{C_6H_2}$), 130.2 (d, $^{3}J_{\mathrm{CP}}=3.9$ Hz; 3,5-$\mathrm{C_6H_2}$), 129.7 (d, $^{1}J_{\mathrm{CP}}=11.6$ Hz; $\mathrm{PC_{mes}}$), 96.2 (d, $^{2}J_{\mathrm{CP}}=6.3$ Hz; $\mathrm{PC{\equiv}C}$), 83.3 (d, $^{1}J_{\mathrm{CP}}=13.1$ Hz; $\mathrm{PC{\equiv}}C$), 23.1 (d, $^{2}J_{\mathrm{CP}}=14.1$ Hz; o-$\mathrm{CH_3}$), 20.7 ppm (s; p-$\mathrm{CH_3}$); ^{31}P{^{1}H} ($\mathrm{C_6D_6}$): $\delta=-54.5$ ppm (s); elemental analysis calcd (%) for $\mathrm{C_{20}H_{23}P}$: C 81.60, H 7.87; found: C 81.57, H 7.82.

Synthesis of $[\mathrm{HP}t\mathrm{Bu_3}][\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_3}]$ (10): A solution of **9** (48 mg, 1.6 mmol) in toluene (3 mL) was added to a solution of $\mathrm{B(C_6F_5)_3}$ (83 mg, 1.6 mmol) and PtBu$_3$ (33 mg, 1.6 mmol) in toluene (3 mL) at −35 °C. After 3 h of stirring, the solvent was completely evaporated off. Pentane (6 mL) was then added and the mixture was stirred overnight. A white solid precipitated. The supernatant liquid was removed, and the product was further washed with pentane and dried. The product was recrystallized by layering a benzene solution of the compound with heptane at RT (142 mg, 87 %). The crystalline product was suitable for X-ray diffraction. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): $\delta=6.70$ (s, 4H; Ar-H), 5.04 (d, 1H, $^{1}J_{\mathrm{HP}}=428$ Hz; HP), 2.26 (s, 12H; o-CH_3), 2.19 (s, 6H; p-CH_3), 1.61 ppm (d, 27H, $^{3}J_{\mathrm{HP}}=15.6$ Hz; tBu); ^{11}B{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): $\delta=-20.9$ ppm (s); ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): 148.6 (dm, $^{1}J_{\mathrm{CF}}=240$ Hz; o-$\mathrm{C_6F_5}$), 142.3 (d, $^{2}J_{\mathrm{CP}}=15$ Hz; o-$\mathrm{C_6H_2}$), 138.8 (dm, $^{1}J_{\mathrm{CF}}=246$ Hz; p-$\mathrm{C_6F_5}$), 137.9 (s; p-$\mathrm{C_6H_2}$), 137.1 (dm, $^{1}J_{\mathrm{CF}}=245$ Hz; m-$\mathrm{C_6F_5}$), 132.4 (d, $^{1}J_{\mathrm{CP}}=12$ Hz; i-$\mathrm{C_6H_2}$), 129.9 (d, $^{3}J_{\mathrm{CP}}=4$ Hz; m-$\mathrm{C_6H_2}$), 38.2 (d, $^{1}J_{\mathrm{CP}}=26$ Hz; quaternary tBu), 30.5 (s; tBu), 22.7 (d, $^{3}J_{\mathrm{CP}}=14$ Hz; o-$\mathrm{CH_3}$, Mes), 21.1 ppm (s; p-$\mathrm{CH_3}$, Mes), $\mathrm{C{\equiv}CP}$, $\mathrm{C{\equiv}CB}$ and quaternary $\mathrm{C_6F_5}$ carbon atoms were not observed; ^{19}F NMR ($\mathrm{CD_2Cl_2}$): $\delta=-132.3$ (dm, 6F, $^{3}J_{\mathrm{FF}}=23$ Hz; o-$\mathrm{C_6F_5}$), −164.0 (t, 3F, $^{3}J_{\mathrm{FF}}=20$ Hz; p-$\mathrm{C_6F_5}$), −167.5 ppm (tm, 6F, $^{3}J_{\mathrm{FF}}=20$ Hz; o-$\mathrm{C_6F_5}$); ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): $\delta=61.4$ (s; H$P$$tBu_3$), −52.9 ppm (s; PMes$_2$); elemental analysis calcd (%) for $\mathrm{C_{50}H_{50}BF_{15}P_2}$: C 59.54, H 5.00; found: C 59.27, H 5.02.

Synthesis of $\mathrm{Mes_2PC{\equiv}CB(NCMe)(C_6F_5)_2}$ (11): Compound **9** (37 mg, 0.13 mmol) and PtBu$_3$ (25 mg, 0.12 mmol) were dissolved in toluene (1 mL) and precooled to −35 °C. The phosphine mixture was then added to a precooled solution of $\mathrm{ClB(C_6F_5)_2}$ (95 mg, 0.25 mmol) in toluene (1 mL) at −35 °C to give a red solution. After the reaction was stirred for 1 h, it was evaporated to ≈0.5 mL. Hexanes (6 mL) were added to precipitate a yellow solid ($[\mathrm{HP}t\mathrm{Bu_3}][\mathrm{Cl_2B(C_6F_5)_2}]$), and the mixture was kept at −35 °C for 2 h. This was filtered through Celite to give a red-orange solution of $\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_2}$. After acetonitrile (20 µL) was added, the solution was kept at −35 °C to afford yellowish crystals of the product (43 mg, 53 %). The product crystals were suitable for X-ray diffraction. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): $\delta=6.77$ (d, 4H, $^{4}J_{\mathrm{HP}}=3.0$ Hz; Ar-H), 2.45 (s, 3H; CH_3, NCMe), 2.29 (s, 12H; o-CH_3), 2.22 ppm (s, 6H; p-CH_3); ^{11}B{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): $\delta=-12.6$ ppm (brs); ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): $\delta=148.2$ (dm, $^{1}J_{\mathrm{CF}}=243$ Hz; o-$\mathrm{C_6F_5}$), 142.5 (d, $^{2}J_{\mathrm{CP}}=15$ Hz; o-$\mathrm{C_6H_2}$), 140.7 (dm, $^{1}J_{\mathrm{CF}}=255$ Hz; p-$\mathrm{C_6F_5}$), 138.8 (s; p-$\mathrm{C_6H_2}$), 137.1 (dm, $^{1}J_{\mathrm{CF}}=248$ Hz; m-$\mathrm{C_6F_5}$), 130.4 (d, $^{1}J_{\mathrm{CP}}=10$ Hz; i-$\mathrm{C_6H_2}$), 130.2 (d, $^{3}J_{\mathrm{CP}}=4$ Hz; m-$\mathrm{C_6H_2}$), 115.0 (s, $\mathrm{C{\equiv}N}$), 22.9 (d, $^{3}J_{\mathrm{CP}}=14$ Hz; o-$\mathrm{CH_3}$, Mes), 21.1 (s; p-$\mathrm{CH_3}$, Mes), 3.5 ppm (s; CH_3, NCMe), the quaternary $\mathrm{B(C_6F_5)_2}$ and acetylenic carbon atoms were not observed. ^{19}F NMR ($\mathrm{CD_2Cl_2}$): $\delta=-133.9$ (m, 4F; o-$\mathrm{C_6F_5}$), −157.9 (t, 2F, $^{3}J_{\mathrm{FF}}=20$ Hz; p-$\mathrm{C_6F_5}$), −164.5 ppm (m, 4F; m-$\mathrm{C_6F_5}$); ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): $\delta=-53.0$ pm (s); elemental analysis calcd (%) for $\mathrm{C_{34}H_{25}BF_{10}NP}$: C 60.11, H 3.71, N 2.06; found: C 59.43, H 3.74, N 2.11.

Synthesis of $\mathrm{(C_6F_5)_2B(H)HC{=}C[P(H)Mes_2][(C_6F_5)_2BC{\equiv}CP(H)Mes_2]}$ (12): The procedure described in the synthesis of **11** was followed to generate $\mathrm{Mes_2PC{\equiv}CB(C_6F_5)_2}$ in situ from compound **9** (75 mg, 0.25 mmol), $\mathrm{ClB(C_6F_5)_2}$ (190 mg, 0.50 mmol), and PtBu$_3$ (50 mg, 0.25 mmol) in a toluene/hexanes (1:12, 6.5 mL) mixture. The red-orange solution was transferred to a Schlenk bomb (50 mL) that was subsequently charged with $\mathrm{H_2}$ (ca. 4 atm) through three freeze–pump–thaw cycles. The reaction was kept under $\mathrm{H_2}$ pressure for 2 d, during which time a light yellow precipitate formed. The contents of the bomb was transferred to a vial and the yellow solid was isolated and washed with hexanes. The product was further recrystallized by layering a $\mathrm{CH_2Cl_2}$ solution of the compound with pentane at −35 °C and extensively washed with pentane to yield a white powder (59 mg, 37 %). ^{1}H NMR ($\mathrm{C_6D_5Br}$, 373 K): $\delta=8.90$ (brd, 1H, $^{3}J_{\mathrm{HP}}=78.1$ Hz; $=$CH), 8.14 (d, 1H, $^{1}J_{\mathrm{HP}}=511$ Hz; PH, $\equiv$CPH), 7.72 (brd, 1H, $^{1}J_{\mathrm{HP}}=457$ Hz; PH, $=$CPH), 6.73 (d, 4H, $^{4}J_{\mathrm{HP}}=5.2$ Hz; Ar-H, $\equiv$CPHMes$_2$), 6.54 (brs, 4H; Ar-H, $=$CPHMes$_2$), 3.45 (brs, 1H; BH), 2.27 (s, 12H; o-CH_3, $\equiv$CPHMes$_2$), 2.25 (brs, 12H; o-CH_3, $=$CPHMes$_2$), 2.09 (s, 6H; p-CH_3), 2.05 ppm (s, 6H; p-CH_3); ^{11}B{^{1}H} NMR ($\mathrm{C_6D_5Br}$, 373 K): $\delta=-16.9$ (d, $^{2}J_{\mathrm{BP}}=17$ Hz; B(C$_6$F$_5$)$_2$), −20.3 ppm (brs; BH(C$_6$F$_5$)$_2$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_5Br}$, 273 K): $\delta=147.7$ (dm, $^{1}J_{\mathrm{CF}}=240$ Hz; overlapping signals of o-$\mathrm{C_6F_5}$), 145.2, 142.8, 142.3, 142.2, 142.1, 141.9, 140.8, 136.3 (dm, $^{1}J_{\mathrm{CF}}=248$ Hz; overlapping signals of m-$\mathrm{C_6F_5}$), 111.8 (brs; $\mathrm{Ar_{Mes}}$), 21.5 (brs; $\mathrm{CH_3}$), 20.7, 20.6, 20.5, 20.4, 20.1, a number of carbon signals were hidden underneath the solvent peaks or could not be unambiguously assigned for a spectrum taken at 25 °C; ^{19}F NMR ($\mathrm{C_6D_5Br}$, 373 K): $\delta=-127.0$ (brs, 4F; o-$\mathrm{C_6F_5}$, $\mathrm{B(C_6F_5)_2}$), −130.5 (brs, 4F; o-$\mathrm{C_6F_5}$, $\mathrm{BH(C_6F_5)_2}$), −159.4 (brs, 2F; p-$\mathrm{C_6F_5}$, $\mathrm{B(C_6F_5)_2}$), −163.8 (brs, 2F; p-$\mathrm{C_6F_5}$, $\mathrm{BH(C_6F_5)_2}$), −164.2 (brs, 4F; m-$\mathrm{C_6F_5}$, B ($\mathrm{C_6F_5})_2$), −166.3 ppm (brs, 4F; m-$\mathrm{C_6F_5}$, $\mathrm{BH(C_6F_5)_2}$); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_5Br}$, 373 K): $\delta=-23.3$ (brs; $=$CP), −48.7 ppm (s; $\equiv$CP); elemental analysis calcd (%) for $\mathrm{C_{64}H_{48}B_2F_{20}P_2}$: C 60.03, H 3.78; found: C 59.99, H 3.66.

Synthesis of $[t\mathrm{Bu_2P(H)C{\equiv}CB(C_6F_5)_2}](n\mathrm{BuCH_2CH})[t\mathrm{Bu_2PC{\equiv}CB(C_6F_5)_2}]\text{-}(\mathrm{OMe})$ (14): Predried $\mathrm{CH_3OH}$ (250 µL) was added to a solution of compound **13** (55 mg, 0.049 mmol) in $\mathrm{CH_2Cl_2}$ (8 mL) in a well-dried Schlenk flask. After stirring at RT for 2d, all volatiles were removed in vacuo. The remaining mixture was redissolved in $\mathrm{CH_2Cl_2}$ (5 mL), the solvent evaporated, and the crude product precipitated by addition of pentane (12 mL). Recrystallization by layering a toluene solution of the compound with pentane gave a colorless crystalline product (42 mg, 74 %). The product crystals were suitable for X-ray diffraction. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): $\delta=5.71$ (d, 1H, $^{1}J_{\mathrm{HP}}=465$ Hz; PH), 3.26 (s, 3H; OCH_3), 2.42 (m, 1H; PCH), 1.95 (m, 1H; PCHCH_2), 1.82 (m, 2H; BCH_2), 1.59 (d, 9H, $^{3}J_{\mathrm{HP}}=15.6$ Hz; tBu), 1.50 (d, 9H, $^{3}J_{\mathrm{HP}}=18.8$ Hz; tBu), 1.46 (d, 9H, $^{3}J_{\mathrm{HP}}=18.7$ Hz; tBu), 1.45 (d, 9H, $^{3}J_{\mathrm{HP}}=15.1$ Hz; tBu), 1.43 (m, 1H; PCHCH_2), 1.41 (m, 1H; PCHCH$_2$CH_2), 1.04 (m, 1H; PCHCH$_2$CH_2), 0.82 (m, 1H; PCHCH$_2$CH$_2$CH_2), 0.65 (m, 1H; PCHCH$_2$CH$_2$CH_2), 0.63 ppm (m, 3H; PCHCH$_2$CH$_2$CH$_2$CH_3); ^{11}B NMR ($\mathrm{CD_2Cl_2}$): $\delta=-6.9$ (s; BOCH$_3$), −18.6 ppm (brs; BCH$_2$CHP); ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): $\delta=148.4$ (dm, $^{1}J_{\mathrm{CF}}=245$ Hz; overlapping signals of o-$\mathrm{C_6F_5}$), 139.3 (dm, $^{1}J_{\mathrm{CF}}=253$ Hz; overlapping signals of p-$\mathrm{C_6F_5}$), 137.5 (dm, $^{1}J_{\mathrm{CF}}=248$ Hz; overlapping signals of m-$\mathrm{C_6F_5}$), 123.3 (brs; overlapping signals of i-$\mathrm{C_6F_5}$), 53.0 (s; $\mathrm{OCH_3}$), 39.1 (d, $^{1}J_{\mathrm{CP}}=38.3$ Hz; quaternary tBu), 37.6 (d, $^{1}J_{\mathrm{CP}}=40.1$ Hz; quaternary tBu), 37.3 (d, $^{1}J_{\mathrm{CP}}=34.7$ Hz; PCH), 35.6 (d, $^{1}J_{\mathrm{CP}}=42.5$ Hz;

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quaternary *t*Bu), 35.5 (d, $^{1}J_{CP}=42.5$ Hz; quaternary *t*Bu), 34.7 (d, $^{3}J_{CP}=3.8$ Hz; $PCHCH_2CH_2$), 33.3 (d, $^{2}J_{CP}=1.9$ Hz; $PCHCH_2$), 29.0 (s; *t*Bu), 28.4 (s; *t*Bu), 27.1 (d, $^{2}J_{CP}=1.4$ Hz; *t*Bu), 27.1 (d, $^{2}J_{CP}=1.7$ Hz; *t*Bu), 23.9 (br s; BCH_2), 23.2 (s; $PCHCH_2CH_2CH_2$), 13.9 ppm (s; $PCHCH_2CH_2CH_2CH_3$), the acetylenic carbon atoms were not observed; ^{19}F NMR (CD_2Cl_2): $\delta=-131.9$ (m, 2F; *o*-C_6F_5), −132.2 (m, 2F; *o*-C_6F_5), −134.2 (m, 4F; *o*-C_6F_5), −160.4 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −160.9 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −162.1 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −162.1 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −165.1 (m, 4F; *m*-C_6F_5), −166.4 ppm (m, 4F; *m*-C_6F_5); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=39.3$ (br s; $PCHCH_2B$), 24.4 ppm (s; *P*H); elemental analysis calcd (%) for $C_{51}H_{51}B_2F_{20}OP_2$: C 53.57, H 4.50; found: C 53.83, H 5.00.

Synthesis of {[*t*Bu$_2$PC≡CB(C_6F_5)$_2$](*n*BuCH$_2$CH$_2$)}$_2$ (15): A Schlenk bomb (50 mL) was charged with compound **13** (23 mg, 0.021 mmol) in toluene (1.5 mL). 1-Hexene (1.5 mL, 12.0 mmol) was added by syringe to the bomb, which was then tightly closed and heated at 80 °C for 24 h. The light yellow solution was poured into a vial and hexanes (8 mL) was added to the solution. After standing in a freezer at −35 °C for 3 d, colorless crystals had precipitated. These were isolated, washed with hexanes and dried in vacuo to give the white product as a mixture of two diastereomers (7 mg, 28 %). The crystalline product was suitable for X-ray diffraction studies. Mixture of two diastereomers: ^{1}H NMR (CD_2Cl_2): $\delta=2.59$ (m), 2.42 (m), 2.09 (m), 1.81 (m), 1.57 (d, 18H, $^{3}J_{HP}=14.9$ Hz; *t*Bu), 1.51 (d, 18H, $^{3}J_{HP}=15.3$ Hz; *t*Bu), 1.46 (d, 18H, $^{3}J_{HP}=15.4$ Hz; *t*Bu), 1.41 (m), 1.24 (m), 1.21 (d, 18H, $^{3}J_{HP}=15.0$ Hz; *t*Bu), 0.99 (m), 0.88 (t, $^{3}J_{HH}=7.2$ Hz), 0.73 (t, $^{3}J_{HH}=7.2$ Hz), 0.67 ppm (m); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-18.1$ ppm (br); ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): $\delta=40.3$ (d, $^{1}J_{CP}=37.6$ Hz; quaternary *t*Bu), 39.2 (d, $^{1}J_{CP}=38.2$ Hz; quaternary *t*Bu), 38.5 (d, $^{1}J_{CP}=40.0$ Hz; quaternary *t*Bu), 37.4 (d, $^{1}J_{CP}=39.1$ Hz; quaternary *t*Bu), 34.7, 34.4, 33.1 (s), 32.8 (d, $J_{CP}=9.9$ Hz), 31.6 (d, $J_{CP}=13.2$ Hz), 29.7 (s; *t*Bu), 29.6 (s; *t*Bu), 29.4 (s; *t*Bu), 28.2 (s; *t*Bu), 23.7, 23.5 (s), 22.9 (s), 14.4 (s; CH_3), 14.0 (s; CH_3), 13.9 ppm (s; CH_3); ^{13}C{^{19}F} NMR (CD_2Cl_2): $\delta=148.5$ (s; *o*-C_6F_5), 148.4 (s; *o*-C_6F_5), 148.1 (s; *o*-C_6F_5), 139.1 (s; *p*-C_6F_5), 137.5 (s; *m*-C_6F_5), 137.4 ppm (s; *m*-C_6F_5); ^{19}F NMR (CD_2Cl_2): $\delta=-129.3$ (dm, 4F, $^{3}J_{FF}=20$ Hz; *o*-C_6F_5), −131.2 (dm, 4F, $^{3}J_{FF}=20$ Hz; *o*-C_6F_5), −132.3 (m, 4F; *o*-C_6F_5), −132.7 (dm, 4F, $^{3}J_{FF}=20$ Hz; *o*-C_6F_5), −161.7 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −162.0 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −162.2 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −162.5 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −165.8 (m, 8F; *m*-C_6F_5), −166.2 ppm (m, 8F; *m*-C_6F_5); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=43.0$ (m), 41.3 ppm (s); elemental analysis calcd (%) for $C_{56}H_{60}B_2F_{20}P_2$: C 56.21, H 5.05; found: C 55.68, H 5.25.

Synthesis of [*t*Bu$_2$PC≡CB(C_6F_5)$_2$](*n*BuCH$_2$CH)[*t*Bu$_2$PC≡CB(C_6F_5)$_2$][O(CH$_2$)$_4$] (16): Compound **14** (30 mg) was dissolved in CH_2Cl_2 (10 mL) and THF (0.5 mL). The resulting mixture was left to stand at 25 °C without stirring for 1 d. The solvent was completely evaporated off. Following the addition of a small amount of pentane, the solid product was further dried in vacuo. Recrystallization by layering a CH_2Cl_2 solution of the compound with pentane was performed when further purification was necessary (26 mg, 81 %). Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): $\delta=3.48$ (m, 2H; OCH_2), 2.83 (m, 1H; PCH), 2.20 (m; BCH_2), 1.97 (m, 4H; $PCHCH_2CH_2$, PCH_2), 1.66 (m, 2H; OCH_2CH_2), 1.58 (d, 9H, $^{3}J_{HP}=15.5$ Hz; *t*Bu), 1.52 (d, 9H, $^{3}J_{HP}=15.3$ Hz; *t*Bu), 1.48 (d, 9H, $^{3}J_{HP}=16.5$ Hz; *t*Bu), 1.41 (d, 9H, $^{3}J_{HP}=16.5$ Hz; *t*Bu), 1.14 (m, 2H; PCH_2CH_2), 0.82 (m, 2H; $PCHCH_2CH_2$), 0.71 (t, 3H, $^{3}J_{HH}=7.0$ Hz; CH_3), 0.50 ppm (m; CH_2CH_3); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-7.1$ (s), −18.3 ppm (br s); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta=148.4$ (dm, $^{1}J_{CF}=236$ Hz; *o*-C_6F_5), 139.3 (dm, $^{1}J_{CF}=249$ Hz; *p*-C_6F_5), 137.4 (dm, $^{1}J_{CF}=254$ Hz; *m*-C_6F_5), 123.5 (br s; quaternary C_6F_5), 73.3 (dm, $^{1}J_{CP}=144$ Hz; C≡CP), 71.4 (dm, $^{1}J_{CP}=146$ Hz; C≡CP), 64.2 (s; OCH_2), 41.2 (m; PCH), 39.1 (d, $^{1}J_{CP}=38$ Hz; quaternary *t*Bu), 38.4 (d, $^{1}J_{CP}=38$ Hz; quaternary *t*Bu), 37.1 (d, $^{1}J_{CP}=44$ Hz; quaternary *t*Bu), 36.4 (d, $^{1}J_{CP}=45$ Hz; quaternary *t*Bu), 34.3 (s; OCH_2CH_2), 34.2 (d, $^{2}J_{CP}=10$ Hz; PCH_2CH_2), 31.7 (s; $PCHCH_2CH_2$), 29.7 (s; *t*Bu), 29.3 (s; *t*Bu), 27.2 (s; *t*Bu), 26.9 (s; *t*Bu), 24.7 (d, $^{2}J_{CP}=6$ Hz; BCH_2), 23.6 (s; $CH_2CH_2CH_3$), 18.5 (d, $^{1}J_{CP}=49$ Hz; PCH_2), 13.8 ppm (s; CH_3); ^{19}F NMR (CD_2Cl_2): $\delta=-131.6$ (m, 2F; *o*-C_6F_5), −132.1 (d, 2F, $^{3}J_{FF}=21$ Hz; *o*-C_6F_5), −134.2 (d, 4F, $^{3}J_{FF}=22$ Hz; *o*-C_6F_5), −161.6 (t, 2F, $^{3}J_{FF}=21$ Hz; *p*-C_6F_5), −161.9 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −162.1 (t, 1F, $^{3}J_{FF}=21$ Hz; *p*-C_6F_5), −165.5 (m, 2F; *m*-C_6F_5), −165.8 (m, 2F; *m*-C_6F_5), −166.5 (m, 2F; *m*-C_6F_5), −166.7 ppm (m, 2F; *m*-C_6F_5); ^{31}P{^{1}H} NMR (CD_2Cl_2): 40.6 (br s), 38.2 ppm (s); IR (thin film from CH_2Cl_2): $\tilde{\nu}=2126$ (C≡C); elemental analysis calcd (%) for $C_{54}H_{56}B_2F_{20}OP_2$: C 54.75, H 4.76; found: C 54.69, H 4.92.

Synthesis of {[*t*Bu$_2$PC≡CB(C_6F_5)$_2$][O(CH$_2$)$_4$]}$_2$ (17): A mixture of B(C_6F_5)$_3$ (18 mg, 0.035 mmol) and P*t*Bu$_3$ (7 mg, 0.035 mmol) dissolved in toluene (1.0 mL) was added to a solution of **5** (18 mg, 0.035 mmol) in toluene (1.0 mL). The reaction mixture immediately turned orange-yellow and became cloudy after stirring for 10 min. Hexanes were added and the reaction was left to stand at −35 °C for 30 min. The mixture was then filtered through Celite and washed with cold hexanes. More hexanes were added to the combined filtrate to a total amount of 18 mL (approximately 2 mM of the (C_6F_5)$_2$BC≡CP*t*Bu$_2$ species). Upon addition of THF (40 μL), the solution immediately turned colorless. The reaction was kept at 25 °C without stirring until a colorless crystalline material precipitated out (typically 2 d). The product was washed with pentane and dried in vacuo (8 mg, 39 %). Single crystals suitable for X-ray diffraction were obtained from the reaction mixture. ^{1}H NMR (CD_2Cl_2): $\delta=3.55$ (t, 4H, $^{3}J_{HH}=5.93$ Hz; CH_2OB), 2.22 (m, 4H; PCH_2), 1.96 (m, 4H; $PCH_2CH_2CH_2$), 1.75 (m, 4H; PCH_2CH_2), 1.38 ppm (d, 36H, $^{3}J_{HP}=16.4$ Hz; *t*Bu); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-7.3$ ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2): 148.4 (dm, $^{1}J_{CF}=240$ Hz; *o*-C_6F_5), 139.4 (dm, $^{1}J_{CF}=246$ Hz; *p*-C_6F_5), 137.3 (dm, $^{1}J_{CF}=245$ Hz; *m*-C_6F_5), 69.9 (d, $^{1}J_{CP}=149$ Hz; C≡*C*P), 65.5 (s; $BOCH_2$), 36.4 (d, $^{1}J_{CP}=44.7$ Hz; quaternary *t*Bu), 33.6 (d, $^{3}J_{CP}=13.7$ Hz; $PCH_2CH_2CH_2$), 27.0 (s; *t*Bu), 25.1 (d, $^{2}J_{CP}=6.4$ Hz; PCH_2CH_2), 18.2 ppm (d, $^{1}J_{CP}=48.7$ Hz; PCH_2), the *i*-C_6F_5 and C≡CB carbon atoms were not observed; ^{19}F NMR (CD_2Cl_2): $\delta=-134.0$ (dm, 16F, $^{3}J_{FF}=24$ Hz; *o*-C_6F_5), −161.6 (t, 8F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −166.2 ppm (m, 16F; *m*-C_6F_5); ^{31}P{^{1}H} NMR (CD_2Cl_2): 38.1 ppm (s); elemental analysis calcd (%) for $C_{52}H_{52}B_2F_{20}O_2P_2$: C 53.27, H 4.47; found: C 53.36, H 3.95.

Synthesis of {[Mes$_2$PC≡CB(C_6F_5)$_2$](CH=CPh)}$_2$ (18): The procedure described in the synthesis of **11** was followed to generate Mes$_2$PC≡CB(C_6F_5)$_2$ in situ from compound **9** (26 mg, 0.088 mmol), ClB(C_6F_5)$_2$ (68 mg, 0.18 mmol), and P*t*Bu$_3$ (18 mg, 0.089 mmol) in a toluene/hexanes (1:12, 6.5 mL) mixture. Phenylacetylene (100 μL, 0.91 mmol) was syringed into the reaction in one portion. After stirring at RT for 30 min, the solvent was evaporated off, and pentane was added to precipitate the product. The yellow product was further recrystallized by layering a CH_2Cl_2 solution of the compound with pentane at RT (18 mg, 28 %). Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): $\delta=9.07$ (d, 2H, $^{3}J_{HP}=40.3$ Hz; C*H*), 6.83 (m, 18H; Ph, Mes), 2.35 (s, 24H; *o*-C*H*$_3$), 2.27 ppm (s, 12H; *p*-C*H*$_3$); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-19.4$ ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): $\delta=144.0$ (d, $^{4}J_{CP}=2.8$ Hz; *p*-C_6H_2), 143.1 (d, $^{2}J_{CP}=10.3$ Hz; *o*-C_6H_2), 132.0 (d, $^{3}J_{CP}=11.5$ Hz; *m*-C_6H_2), 130.3 (d, $J_{CP}=5.3$ Hz; Ph), 128.0 (d, $J_{CP}=2.9$ Hz; Ph), 127.2 (d, $J_{CP}=1.5$ Hz; Ph), 120.5 (d, $^{1}J_{CP}=91$ Hz; *i*-C_6H_2), 23.8 (d, $^{3}J_{CP}=6.2$ Hz; *o*-CH_3, Mes), 21.3 ppm (s; *p*-CH_3, Mes); ^{13}C{^{19}F} NMR (CD_2Cl_2): $\delta=147.7$ (s; *o*-C_6F_5), 139.0 (s; *p*-C_6F_5), 136.9 ppm (s; *m*-C_6F_5), a cross-peak for =CHB carbon was observed in an HSQC experiment at 177.5 ppm; ^{19}F NMR (CD_2Cl_2): $\delta=-132.5$ (dm, 8F, $^{3}J_{FF}=20$ Hz; *o*-C_6F_5), −162.3 (t, 4F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −166.5 ppm (m, 8F; *m*-C_6F_5); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=-4.7$ ppm (s); elemental analysis calcd (%) for $C_{80}H_{56}B_2F_{20}P_2$: C 64.89, H 3.81; found: C 62.85, H 4.08.

Synthesis of (C_6F_5)$_2$BC(H)=C[P(H)*t*Bu$_2$](AlCl$_3$) (19): A solution of **5** (75 mg, 0.15 mmol) in toluene (4 mL) was added to a stirring suspension of AlCl$_3$ (19 mg, 0.14 mmol) in toluene (4 mL). The reaction was stirred overnight at RT. After passing the reaction mixture through a plug of Celite, the solvent was evaporated from the filtrate. Recrystallization by layering a toluene solution of the compound with hexanes gave a white solid that was further washed with hexanes and dried in vacuo (67 mg, 74 %). Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with hexanes at 25 °C. ^{1}H NMR (CD_2Cl_2, 298 K): $\delta=8.23$ (d, 1H, $^{3}J_{HP}=45.9$ Hz; =C*H*), 5.42 (d, 1H, $^{1}J_{HP}=429$ Hz; P*H*), 1.51 ppm (d, 18H, $^{3}J_{HP}=16.5$ Hz; *t*Bu$_2$); ^{11}B{^{1}H} NMR (CD_2Cl_2, 298 K): $\delta=12.6$ ppm (br s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K; partial): $\delta=186.9$ (br s; =CH), 148.4 (dm, $^{1}J_{CF}=245$ Hz; *o*-C_6F_5), 141.7 (dm, $^{1}J_{CF}=253$ Hz; *p*-C_6F_5), 137.8 (dm, $^{1}J_{CF}=250$ Hz; *m*-

C_6F_5), 34.7 (d, $^{1}J_{CP}=35$ Hz; quaternary *t*Bu), 28.5 (s; *t*Bu), the *i*-C_6F_5 and C≡CAl carbon resonances were not observed; ^{19}F NMR (CD_2Cl_2, 193 K): $\delta=-130.1$ (dm, 4F, $^{3}J_{FF}=20$ Hz; *o*-C_6F_5), −155.3 (t, 2F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −163.9 ppm (m, 4F; *m*-C_6F_5); ^{27}Al NMR (CD_2Cl_2, 298 K): $\delta=$ 103.8 ppm (s); ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): $\delta=76.9$ ppm (br s); elemental analysis calcd (%) for $C_{22}H_{20}AlBCl_3F_{10}P$: C 41.37, H 3.16; found: C 41.05, H 3.74.

Synthesis of $(C_6F_5)_2$BC(H)=C[P(H)*t*Bu$_2$](AlBr$_3$) (20): $AlBr_3$ (30 mg, 0.11 mmol) in toluene (1.0 mL) was added to compound **5** (58 mg, 0.11 mmol) dissolved in toluene (2.0 mL) at −35 °C, and the mixture was stirred at that temperature for 5 min. The reaction was warmed up to RT and stirred for a further 30 min. The precipitated product was separated on a filter frit and washed with toluene followed by pentane. The product was then dried in vacuo (42 mg, 48 %). Single crystals suitable for X-ray diffraction were grown from a solution of the compound in bromobenzene at 25 °C. ^{1}H NMR (C_6D_5Br): $\delta=7.87$ (d, 1H, $^{3}J_{HP}=45.0$ Hz; =C*H*), 4.94 (d, 1H, $^{1}J_{HP}=432$ Hz; P*H*), 1.12 ppm (d, 18H, $^{3}J_{HP}=16.2$ Hz; *t*Bu$_2$); ^{11}B NMR (C_6D_5Br): no signal observed; ^{13}C{^{1}H} NMR (C_6D_5Br): $\delta=$ 147.4 (dm, $^{1}J_{CF}=248$ Hz; *o*-C_6F_5), 140.8 (dm, $^{1}J_{CF}=260$ Hz; *p*-C_6F_5), 136.7 (dm, $^{1}J_{CF}=247$ Hz; *m*-C_6F_5), 114.2 (br s; *i*-C_6F_5), 33.6 (d, $^{1}J_{CP}=33$ Hz; quaternary *t*Bu), 27.3 (s; *t*Bu), the olefinic carbon resonances were not observed; ^{19}F NMR (C_6D_5Br): $\delta=-127.7$ (dm, 4F, $^{3}J_{FF}=23$ Hz; *o*-C_6F_5), −152.5 (br s, 2F; *p*-C_6F_5), −162.1 ppm (m, 4F; *m*-C_6F_5); ^{27}Al NMR (C_6D_5Br): $\delta=81.0$ ppm (s); ^{31}P{^{1}H} NMR (C_6D_5Br): $\delta=84.5$ (br s); elemental analysis calcd (%) for $C_{22}H_{20}AlBBr_3F_{10}P$: C 33.75, H 2.57; found: C 34.10, H 2.68.

Synthesis of $(C_6F_5)_3$BC(H)=C[P(H)*t*Bu$_2$][Zn(C_6F_5)] (21): Compound **5** (29 mg, 0.056 mmol) and [Zn$(C_6F_5)_2$]·C_7H_8 (28 mg, 0.056 mmol) were stirred together in CH_2Cl_2 (2 mL) overnight at RT. Evaporation of the solvent afforded a white solid product (36 mg, 70 %). Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with pentane at 25 °C. ^{1}H NMR (CD_2Cl_2): $\delta=8.92$ (d, 1H, $^{3}J_{HP}=46$ Hz; C=C*H*), 5.28 (d, 1H, $^{1}J_{HP}=425$ Hz; P*H*), 1.36 ppm (d, 18H, $^{3}J_{HP}=15.7$ Hz; *t*Bu); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta=-12.9$ ppm (d, $^{3}J_{BP}=$ 20 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): $\delta=149.2$ (dm, $^{1}J_{CF}=234$ Hz; *o*-C_6F_5, [Zn(C_6F_5)]), 148.8 (dm, $^{1}J_{CF}=241$ Hz; *o*-C_6F_5, B$(C_6F_5)_3$), 142.2 (dm, $^{1}J_{CF}=260$ Hz; *p*-C_6F_5, [Zn(C_6F_5)]), 140.4 (dm, $^{1}J_{CF}=241$ Hz; *p*-C_6F_5, B$(C_6F_5)_3$), 138.1 (dm, $^{1}J_{CF}=246$ Hz; *m*-C_6F_5, B$(C_6F_5)_3$), 137.5 (dm, $^{1}J_{CF}=$ 254 Hz; *m*-C_6F_5, [Zn(C_6F_5)]), 33.7 (d, $^{1}J_{CP}=38$ Hz, quaternary *t*Bu), 28.0 ppm (s; *t*Bu), the *i*-C_6F_5 and olefinic carbon atoms were not observed; ^{19}F NMR (CD_2Cl_2): $\delta=-117.5$ (d, 2F, $^{3}J_{FF}=21$ Hz; *o*-C_6F_5, [Zn(C_6F_5)]), −130.4 (d, 6F, $^{3}J_{FF}=21$ Hz; *o*-C_6F_5, B$(C_6F_5)_3$), −151.7 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5, [Zn(C_6F_5)]), −158.8 (t, 3F, $^{3}J_{FF}=21$ Hz; *p*-C_6F_5, B$(C_6F_5)_3$), −160.5 (m, 2F; *m*-C_6F_5, [Zn(C_6F_5)]), −163.6 ppm (m, 6F; *m*-C_6F_5, B$(C_6F_5)_3$); ^{31}P{^{1}H} (CD_2Cl_2): $\delta=73.6$ ppm (br s); elemental analysis calcd (%) for $C_{34}H_{20}BF_{20}PZn$: C 44.60, H 2.20; found: C 44.90, H 2.42.

Synthesis of $(C_6F_5)_3$BC(H)=C[P(H)*t*Bu$_2$][Al$(C_6F_5)_2$] (22): In a small vial, compound **5** (30 mg, 0.058 mmol) was dissolved in bromobenzne (1.0 mL) and the solution was layered with a solution of [Al$(C_6F_5)_3$]·toluene (36 mg, 0.068 mmol) in benzene (2.0 mL). After 4 d standing at RT without stirring, a microcrystalline solid product had precipitated. The mother liquor was pipetted off, and the product was washed with benzene and pentane, followed by drying in vacuo (37 mg, 61 %). Single crystals suitable for X-ray diffraction were obtained from the reaction mixture. ^{1}H NMR (C_6D_5Br): $\delta=9.43$ (br d, 1H, $^{3}J_{HP}=$ 51.2 Hz; =C*H*), 4.75 (d, 1H, $^{1}J_{HP}=423$ Hz; P*H*), 0.94 ppm (d, 18H, $^{3}J_{HP}=$ 16.1 Hz; *t*Bu$_2$); ^{11}B NMR (C_6D_5Br): $\delta=-13.8$ ppm (s); ^{13}C{^{1}H} NMR (C_6D_5Br): $\delta=27.1$ (br s; *t*Bu), all other carbon resonances were not observed due to low solubility of the compound in C_6D_5Br; more polar solvents were not suitable as they reacted with the compound; ^{19}F NMR (C_6D_5Br): $\delta=-121.3$ (br s, 4F; *o*-C_6F_5), −131.0 (br s, 6F; *o*-C_6F_5), −147.8 (br s, 2F; *p*-C_6F_5), −156.9 (br s, 3F; *p*-C_6F_5), −158.3 (br s, 4F; *m*-C_6F_5), −161.8 ppm (br s, 6F; *m*-C_6F_5); ^{27}Al NMR (C_6D_5Br): no signal observed; ^{31}P{^{1}H} NMR (C_6D_5Br): no signal observed; elemental analysis calcd (%) for $C_{44}H_{29}AlBF_{25}P$: C 47.98, H 2.65; found: C 46.28, H 3.01.

Synthesis of [$(C_6F_5)_2$B]$_2$HC≡CH[P(H)*t*Bu$_2$] (23): Compound **5** (100 mg, 0.19 mmol) and HB$(C_6F_5)_2$ (67 mg, 0.19 mmol) were stirred in toluene (5 mL) at 25 °C overnight. The solvent was then completely evaporated off, and the residue was stirred in hexanes (6 mL) overnight. The white solid product was isolated, washed with haxanes, and dried in vacuo (113 mg, 68 %). Single crystals suitable for X-ray diffraction were grown by layering a solution of the product in CH_2Cl_2 with hexanes at 25 °C. ^{1}H NMR (CD_2Cl_2, 298 K): $\delta=4.61$ (dd, 1H, $^{1}J_{HP}=433$ Hz, $^{3}J_{HH}=12.7$ Hz; P*H*), 3.39 (dd, 1H, $^{3}J_{HP}=16.5$ Hz, $^{3}J_{HH}=11.7$ Hz; C*H*[B$(C_6F_5)_2$]$_2$), 2.44 (t, 1H, $^{3}J_{HH}=12.0$ Hz; C*H*PH*t*Bu$_2$), 1.52 (d, 9H, $^{3}J_{HP}=15.9$ Hz; *t*Bu), 1.43 ppm (d, 9H, $^{3}J_{HP}=15.6$ Hz; *t*Bu); ^{11}B{^{1}H} NMR (CD_2Cl_2, 298 K): $\delta=$ 60.5 (br s), −15.9 ppm (s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, partial): $\delta=$ 143.1 (m; *o*-, *p*-, *m*-C_6F_5), 41.6 (s; *C*HPH*t*Bu$_2$), 36.2 (d, $^{1}J_{CP}=35$ Hz; quaternary *t*Bu), 33.9 (d, $^{1}J_{CP}=35$ Hz; quaternary *t*Bu), 28.7 (s; *t*Bu), 27.8 (s; *t*Bu), 13.3 ppm (br s; *C*H[B$(C_6F_5)_2$]$_2$) (the *i*-C_6F_5 carbon atoms were not observed; ^{19}F NMR (CD_2Cl_2, 193 K): $\delta=-126.9$ (dm, 1F, $^{3}J_{FF}=23$ Hz; *o*-C_6F_5), −128.9 (m, 1F; *o*-C_6F_5), −129.8 (m, 2F; *o*-C_6F_5), −130.2 (br s, 1F; *o*-C_6F_5), −132.3 (br s, 1F; *o*-C_6F_5), −132.9 (m, 1F; *o*-C_6F_5), −133.6 (dm, 1F, $^{3}J_{FF}=23$ Hz; *o*-C_6F_5), −152.5 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −152.8 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −156.9 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −159.3 (t, 1F, $^{3}J_{FF}=20$ Hz; *p*-C_6F_5), −161.1 (br s, 1F; *m*-C_6F_5), −162.3 (br s, 1F; *m*-C_6F_5), −162.6 (m, 1F; *m*-C_6F_5), −163.0 (m, 2F; *m*-C_6F_5), −163.2 (m, 1F; *m*-C_6F_5), −164.1 (m, 1F; *m*-C_6F_5), −166.4 ppm (m, 1F; *m*-C_6F_5); ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): $\delta=55.6$ ppm (s); elemental analysis calcd (%) for $C_{34}H_{21}B_2F_{20}P$: C 47.37, H 2.46; found: C 46.77, H 2.36.

X-ray crystallography: Crystals were coated in paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer employing $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Data collection strategies were determined by using Bruker Apex software and optimized to provide >99.5 % complete data to a 2θ value of at least 55°. The data were collected at 150(±2) K for all crystals. The frames were integrated with the Bruker SAINT software package by using a narrow-frame algorithm. Data were corrected for absorption effects by using the empirical multiscan method (SADABS). Nonhydrogen atomic scattering factors were taken from the literature tabulations. The heavy-atom positions were determined by using direct methods employing the SHELXTL direct-methods routine. The remaining nonhydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function ω-$(F_o-F_c)^2$ in which the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all nonhydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter case atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bound assuming a C−H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C atom to which they are bound. The H atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation, as well as the magnitude of the residual electron densities in each case, were of no chemical significance. CCDC-768761 (**10**), 808763 (**12**), 808764 (**11**), 808765 (**14**), 808766 (**15**), 808767 (**16**), 808768 (**17**), 808769 (**18**), 808770 (**2**), 808771 (**19**), 808772 (**21**), 808773 (**20**), 808774 (**23**), 808775 (**22**), 808776 (**3**), 808777 (**4**), 808778 (**8**), and 808779 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

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