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Deprotonation and Addition Reactions of Frustrated Lewis Pairs with Alkynes

Meghan A. Dureen, Christopher C. Brown, and Douglas W. Stephan*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada, M5S 3H6

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Deprotonation of terminal alkynes is effected by the treatment with tBu$_3$P and B(C$_6$F$_5$)$_3$ to give [tBu$_3$PH][PhCCB(C$_6$F$_5$)$_3$] (**1a**) and [tBu$_3$PH][RCCB(C$_6$F$_5$)$_3$] (R = nBu **2**, tBu **3**, Me$_3$Si **4**, and CpFe(C$_5$H$_4$) **5**). In a similar fashion, FLP deprotonation of 1,4-diethynylbenzene was employed to prepare the salt [tBu$_3$PH]$_2$[(C$_6$F$_5$)$_3$BCC(C$_6$H$_4$)CCB(C$_6$F$_5$)$_3$] (**6**). As well, use of differing Lewis acids afforded the species [tBu$_3$PH][PhCCEAr$_3$] (EAr$_3$ = Al(C$_6$F$_5$)$_3$ **7**, PhB(C$_6$F$_5$)$_2$ **8**, BPh$_3$ **9**). The corresponding reaction of Me$_3$SiCCSiMe$_3$ afforded [tBu$_3$PSiMe$_3$][Me$_3$SiCCB(C$_6$F$_5$)$_3$] (**10**). For less basic phosphines, phosphine/borane addition reactions were observed with alkynes. Thus the species E-R$_3$P(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (R = o-tol **11**, Ph **12**) were prepared. In the latter case, Ph$_3$P·B(C$_6$F$_5$)$_3$ was employed. Similarly, E-Ph$_3$P(CpFe(C$_5$H$_4$))C=C(H)B(C$_6$F$_5$)$_3$ (**13**), E-Ph$_3$P(Ph)C=C(Me)B(C$_6$F$_5$)$_3$ (**14**), E-R$_2$PH(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (R = Ph **15**, C$_6$H$_2$Me$_3$ **16**), and E-(C$_6$H$_2$$tBu_3$)PH$_2$(Ph)C=C(H)B(C$_6F_5$)$_3$ (**17**) were prepared. Again, variation in the Lewis acid afforded E-Ph$_3$P(Ph)C=C(H)EAr$_3$ (EAr$_3$ = PhB(C$_6$F$_5$)$_2$ **18**, Al(C$_6$F$_5$)$_3$ **19**), E-Ph$_3$P(nBu)C=C(H)Al(C$_6$F$_5$)$_3$ (**20**), and E-(o-tol)$_3$P(Ph)C=C(H)Al(C$_6$F$_5$)$_3$ (**21**). The macrocyclic [(H)C=C(Ph)Mes$_2$PC$_6$F$_4$B(C$_6$F$_5$)$_2$]$_2$ (**22**) was prepared from the analogous alkyne addition to Mes$_2$PC$_6$F$_4$B(C$_6$F$_5$)$_2$, while E-Ph$_2$PCH$_2$CH$_2$PPh$_2$-(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (**23**) and E-(CH$_2$PPh$_2$(Ph)C=C(H)B(C$_6$F$_5$)$_3$)$_2$ (**24**) were derived from the reactions of Ph$_2$PCH$_2$CH$_2$PPh$_2$. The related addition reaction involving 1,4-diethynylbenzene gave E-HC≡CC$_6$H$_4$C(PPh$_3$)=C(H)B(C$_6$F$_5$)$_3$ (**25**), while subsequent reaction with tBu$_3$P and B(C$_6$F$_5$)$_3$ yielded the unusual salt/zwitterion [tBu$_3$PH][(C$_6$F$_5$)$_3$BCC≡C$_6$H$_4$C(PPh$_3$)=C(H)-B(C$_6$F$_5$)$_3$] (**26**). Reaction of PhCH$_2$NMe$_2$ with PhCCH and B(C$_6$F$_5$)$_3$ gave give a 84:16 mixture of [PhCH$_2$NMe$_2$H][PhCCB(C$_6$F$_5$)$_3$] (**27a**) and PhCH$_2$NMe$_2$(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (**27b**), while imines were used to prepare [(tBu)HN=CHPh][PhCCB(C$_6$F$_5$)$_3$] (**28**) and [(tBu)HN=CPh$_2$][PhCCB(C$_6$F$_5$)$_3$] (**29**). The corresponding reaction of tBuNCNtBu, B(C$_6$F$_5$)$_3$, and two equivalents of PhCCH led to the unusual product [tBuNCN(H)C(Ph)=C(H)tBu][PhCCB(C$_6$F$_5$)$_3$] (**30**). Finally, non-pnictogen Lewis bases were explored. The reaction of the N-heterocyclic carbene ItBu with B(C$_6$F$_5$)$_3$ and PhCCH was shown to yield the deprotonation product [ItBuH][PhCCB(C$_6$F$_5$)$_3$] (**31**), while the sulfides R$_2$S gave E-R$_2$S(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (R = Me **32**, PhCH$_2$ **33**). The formation of these latter sulfide zwitterions was demonstrated to be reversible.

Introduction

Alkyne activation by transition metals is an important reaction in the synthetic toolbox of organic chemists.[1] Metalations of terminal alkynes provide useful synthons, while transition metal-catalyzed reactions allow a variety of C−C coupling reactions including oxidative dimerizations,[2] alkyne-arene coupling reactions,[3] and alkynylations of aldehydes.[4] Similarly, the utility of borane reagents in the organic manipulation of alkynes, whether via vinyl boranes, alkynyl boranes, alkynyl borates, or a myriad of other synthons, is also well established.[5−7] Of particular relevance to the present work is the utility of B(C$_6$F$_5$)$_3$ in mediating the catalytic hydrostannation[8] or hydrogermylation[9] of alkynes as well as the intramolecular addition of silyl enol ethers to alkynes.[10] In related reactivity Erker and co-workers have reported the cyclization of dialkynylsilanes employing

*To whom correspondence should be addressed. E-mail: dstephan@chem.utoronto.ca.

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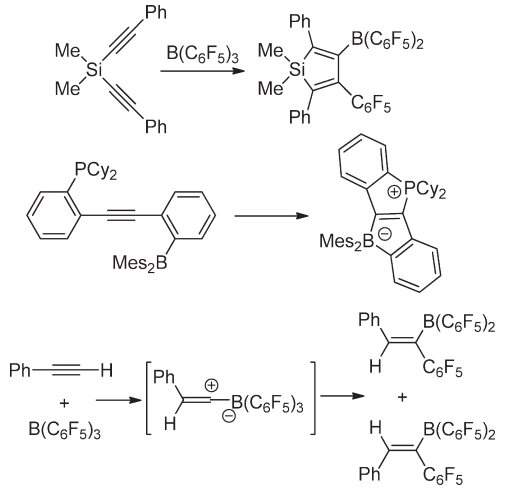
Scheme 1. Reactions of $B(C_6F_5)_3$ and Alkynes



$B(C_6F_5)_3$ (Scheme 1); however this reaction is believed to proceed by abstraction of an acetylide from the Si center rather than electrophilic attack of the borane on the π bond.[11] This latter reaction is thought to be analogous to the reactivity of BEt_3 with dialkyl stannanes and silanes,[12] and similar reactivity has also led to the synthesis of a variety of interesting group IV zwitterions from the reaction of metal alkyne complexes with $B(C_6F_5)_3$.[13−16]

In our own chemistry we have been exploring the activation of a variety of small molecules employing combinations of electrophilic and nucleophilic reagents that act simultaneously or sequentially on a substrate by exploiting steric congestion to preclude the direct reaction of the electrophile and nucleophile. Remarkably, such *frustrated Lewis pairs* (FLPs)[17−19] comprised of a sterically encumbered phosphine,[20,21] imine,[22,23] or carbene[24,25] and an electron-deficient borane were initially shown to effect the heterolytic activation of H_2 and effect metal-free catalytic hydrogenations.[22,2326−29] FLPs have also been shown to react with a variety of other small molecules including THF,[30,31] catechol borane,[32] terminal olefins,[33] dienes,[34] CO_2,[35,36] N_2O,[37,38] and CO.[39] We have also previously communicated the reactivity of terminal alkynes with phosphine/Lewis acid combinations. In these cases, two courses of reactions were observed, either deprotonation of the alkyne derivatives to give phosphonium alkynyl-borates or addition reactions affording zwitterionic, alkenyl-phosphonium borate salts. In the latter case, analogous reactivity has been exploited by Yamaguchi and co-workers[40] to effect intramolecular addition of phosphines and boranes, affording interesting electronic materials (Scheme 1). Subsequently, Berke and co-workers described the related reactions of the FLP system with acetylene and other alkynes[41] and also identified the products of reaction of $B(C_6F_5)_3$ and alkyne alone (Scheme 1). In this paper, we expand the scope and explore the features of this FLP reactivity with alkynes developing a broader sense of how this reactivity applies to a range of terminal alkynes and nucleophiles including phosphines, nitrogen bases, carbenes, and thioethers.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing a Vacuum Atmospheres glovebox and a Schlenk-type vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentane, toluene, CH_2Cl_2) or were dried over the appropriate agents and distilled into the same kind of storage flasks (C_6H_5Br). All solvents were thoroughly degassed after purification (repeated freeze−pump−thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks, and degassed accordingly (C_6D_5Br, CD_2Cl_2). Toluene and pentane were stored over potassium mirrors, while bromobenzene and CH_2Cl_2 were stored over 4 Å molecular sieves. ^1H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded at 25 °C on Varian 300 and 400 MHz and Bruker 400 MHz spectrometers. Chemical shifts are

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given relative to $SiMe_4$ and referenced to the residual solvent signal (^1H, ^{13}C) or relative to an external standard (^{11}B: $Et_2O \cdot BF_3$; ^{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 (δ) are reported in ppm, and coupling constants (J) as scalar values in Hz. Combustion analyses were performed in-house employing a Perkin-Elmer CHN analyzer. Tris(pentafluorophenyl)borane was generously donated by NOVA Chemicals Corporation; tBu$_3$P was purchased from Strem Chemicals; all other reagents were purchased from Aldrich. Phenylacetylene was vacuum transferred from $CaCl_2$ and stored at −35 °C in the glovebox. Liquids were stored over 4 Å molecular sieves. (PhMe)·Al$(C_6F_5)_3$,[42] Mes_2PH,[43] PhB$(C_6F_5)_2$,[44] $Mes_2PC_6F_4B(C_6F_5)_2$,[45] $Ph_2C{=}NtBu$,[46] and $Ph_3P \cdot B(C_6F_5)_3$[47−49] were prepared following literature methods.

Synthesis of [*t*Bu$_3$PH][RCCB(C$_6$F$_5$)$_3$] (R = Ph (1a), C$_4$H$_9$ (2), *t*Bu (3), Me$_3$Si (4), and CpFe(C$_5$H$_4$) (5)), [*t*Bu$_3$PH]$_2$[1,4-C$_6$H$_4$-(CCB(C$_6$F$_5$)$_3$)$_2$] (6), and [*t*Bu$_3$PH][PhCCEAr$_3$] (EAr$_3$ = Al-(C$_6$F$_5$)$_3$ (7), BPh(C$_6$F$_5$)$_2$ (8), BPh$_3$ (9)). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. A solution of PhC≡CH (75 mg, 1.5 mmol) and tBu$_3$P (303 mg, 1.5 mmol) in toluene (10 mL) was cooled to −35 °C, at which point $B(C_6F_5)_3$ (767 mg, 1.5 mmol) was added in one portion, and the solution was shaken, not stirred, until all of the borane had dissolved and a yellowish oil separated from the toluene layer. This toluene layer was decanted and the oil dried under reduced pressure to afford a yellowish solid. Recrystallization from PhCl (2 mL) afforded a colorless, crystalline solid (805 mg, 75%), and layering of the supernatant PhCl with pentane (3 mL) afforded an additional 75 mg of product for an overall yield of 82%.

1: ^1H NMR (CD_2Cl_2): 7.32 (m, 2H, *o*-Ph), 7.21 (tt, 2H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz, *m*-Ph), 7.15 (tt, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz, *p*-Ph), 4.80 (d, 1H, $^1J_{H-P}$ = 428 Hz, tBu$_3$P*H*), 1.52 (d, 27H, $^3J_{H-P}$ = 16 Hz, t*Bu*$_3$PH). ^{11}B NMR (CD_2Cl_2): −20.78 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 148.85 (dm, $^1J_{C-F}$ = 245 Hz, *o*-C_6F_5), 138.88 (dm, $^1J_{C-F}$ = 248 Hz, *p*-C_6F_5), 137.18 (dm, $^1J_{C-F}$ = 241 Hz, *m*-C_6F_5), 131.80, 128.62, 128.19 (s, *ipso*-Ph), 126.64, 37.98 (d, $^1J_{C-P}$ = 27 Hz, P*C*Me$_3$), 30.25 (s, PC*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −132.73 (d, 6F, $^3J_{F-F}$ = 25 Hz, *o*-C_6F_5), −163.94 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.45 (d, 6F, $^3J_{F-F}$ = 19 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 61.49. Anal. Calcd for $C_{38}H_{33}BF_{15}P$ (816.443): C, 55.90; H, 4.07. Found: C, 55.88; H, 4.18. X-ray quality crystals were grown by slow cooling of a solution in chlorobenzene.

2: white solid, 117 mg, 81%. ^1H NMR (C_6D_5Br): 4.3 (d, 1H, $^1J_{H-P}$ = 434 Hz, tBu$_3$P*H*), 2.2 (t, 2H, $^3J_{H-H}$ = 7 Hz, CH_2CCB), 1.6−1.3 (m, 4H, $CH_3CH_2CH_2$), 0.95 (d, 27H, $^3J_{H-P}$ = 15 Hz, t*Bu*$_3$PH), 0.8 (t, 3H, $^3J_{H-H}$ = 7 Hz, CH_3CH$_2$). ^{11}B NMR (C_6D_5Br): −20.5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 148.3 (dm, $^1J_{C-F}$ = 237 Hz, *o*-C_6F_5), 138.2 (dm, $^1J_{C-F}$ = 243 Hz, *p*-C_6F_5), 136.8 (dm, $^1J_{C-F}$ = 243 Hz, *m*-C_6F_5), 37.9 (d, $^1J_{C-P}$ = 26 Hz, P*C*Me$_3$), 32.1 (s), 30.2 (s, PC*Me*$_3$), 22.1 (s), 20.1 (s), 13.7 (s). ^{19}F NMR (C_6D_5Br): −130.8 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −163.1 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.1 (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (C_6D_5Br): 60.5 (s). Anal. Calcd for $C_{36}H_{37}BF_{15}P$ (796.453): C, 54.29; H, 4.68. Found: C, 53.72; H, 4.48. X-ray quality crystals were grown by slow cooling of a solution in chlorobenzene.

3: white solid, 81 mg, 52%. ^1H NMR (CD_2Cl_2): 5.0 (d, 1H, $^1J_{H-P}$ = 430 Hz, tBu$_3$P*H*), 1.6 (d, 27H, $^3J_{H-P}$ = 16 Hz, t*Bu*$_3$PH), 1.1 (s, 9H, CC*Me*$_3$). ^{11}B NMR (CD_2Cl_2): −21.0. $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 148.6 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 138.2 (dm, $^1J_{C-F}$ = 238 Hz, *p*-C_6F_5), 136.8 (dm, $^1J_{C-F}$ = 240 Hz, *m*-C_6F_5), 37.9 (d, $^1J_{C-F}$ = 28 Hz, P*C*Me$_3$), 31.6 (s, CC*Me*$_3$), 30.2 (s, PC*Me*$_3$), 28.06 (s, C*C*Me$_3$). ^{19}F NMR (CD_2Cl_2): −132.4 (d, 6F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −164.5 (t, 3F, $^3J_{F-F}$ = 25 Hz, *p*-C_6F_5), −167.7 (t, 3F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 61.7. Anal. Calcd for $C_{36}H_{37}BF_{15}P$ (796.453): C, 54.29; H, 4.68. Found: C, 54.18; H, 4.91.

4: white solid, 100 mg, 63%. ^1H NMR (C_6D_5Br): 4.0 (d, 1H, $^1J_{H-P}$ = 430 Hz, tBu$_3$P*H*), 0.8 (d, 27H, $^3J_{H-P}$ = 16 Hz, t*Bu*$_3$PH), 0.0 (s, 9H, Si*Me*$_3$). ^{11}B NMR (CD_2Cl_2): −20.8. $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 148.8 (dm, $^1J_{C-F}$ = 245 Hz, *o*-C_6F_5), 138.9 (dm, $^1J_{C-F}$ = 236 Hz, *p*-C_6F_5), 137.1 (dm, $^1J_{C-F}$ = 236 Hz, *m*-C_6F_5), 38.3 (d, $^1J_{C-P}$ = 27 Hz, P*C*Me$_3$), 30.6 (s, PC*Me*$_3$), 0.9 (s, Si*Me*$_3$). ^{19}F NMR (C_6D_5Br): −130.4 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −162.9 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.3 (t, 3F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 61.5. Anal. Calcd for $C_{35}H_{37}BF_{15}SiP$ (812.528): C, 51.74; H, 4.59. Found: C, 51.53; H, 4.76.

5: orange, crystalline solid, 216 mg, 95%. ^1H NMR (CD_2Cl_2): 4.9 (d, 1H, $^1J_{H-P}$ = 430 Hz, tBu$_3$P*H*), 4.3 (t, 2H, $^3J_{H-H}$ = 2 Hz, Fe*Cp*′), 4.1 (s, 5H, Fe*Cp*), 4.0 (t, 2H, $^3J_{H-H}$ = 2 Hz, Fe*Cp*′), 1.6 (d, 27H, $^3J_{H-P}$ = 16 Hz, t*Bu*$_3$PH). ^{11}B NMR (CD_2Cl_2): −20.8. $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 148.8 (dm, $^1J_{C-F}$ = 238 Hz, *o*-C_6F_5), 138.8 (dm, $^1J_{C-F}$ = 245 Hz, *p*-C_6F_5), 137.1 (dm, $^1J_{C-F}$ = 248 Hz, *m*-C_6F_5), 71.4 (s, Fe*Cp*′), 70.2 (s, Fe*Cp*), 68.05 (s, Fe*Cp*′), 38.2 (d, J = 27 Hz, P*C*Me$_3$), 30.5 (s, PC*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −132.7 (d, 6F, $^3J_{F-F}$ = 20 Hz, *o*-C_6F_5), −164.3 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.8 (t, 6F, $^3J_{F-F}$ = 18 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 60.8. Anal. Calcd for $C_{42}H_{36}BF_{15}PFe$ (923.357): C, 54.63; H, 3.93. Found: C, 54.63; H, 4.21. X-ray quality crystals were grown by slow cooling of a solution in CH_2Cl_2.

6: off-white powder, 209 mg, 81%. ^1H NMR (CD_2Cl_2): 7.2 (s, 4H, H_{Ar}), 7.37 (m, 2H, *o*-CCPh), 4.7 (d, 2H, $^1J_{H-P}$ = 427 tBu$_3$P*H*), 1.6 (d, 54H, $^3J_{H-P}$ = 16 Hz, t*Bu*$_3$PH). ^{11}B NMR (CD_2Cl_2): −20.9 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 143.2 (dm, $^1J_{C-F}$ = 243 Hz, *o*-C_6F_5), 138.2 (dm, $^1J_{C-F}$ = 244 Hz, *p*-C_6F_5), 136.5 (dm, $^1J_{C-F}$ = 248 Hz, *m*-C_6F_5), 131.0, 125.4 (s, *ipso*-C_{Ar}), 37.4 (d, $^1J_{C-P}$ = 26 Hz, P*C*Me$_3$), 29.8 (s, PC*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −132.5 (d, 6F, $^3J_{F-F}$ = 25 Hz, *o*-C_6F_5), −163.6 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −167.2 (t, 6F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 61.1 Anal. Calcd for $C_{70}H_{60}B_2F_{30}P_2$ (1554.773): C, 54.08; H, 3.89. Found: C, 54.44; H, 4.19. Crystals were grown by slow cooling of a solution in CH_2Cl_2; due to multiple disordered solvent molecules, the structure was not suitable for publication, although connectivity was established.

7: 61 mg (91%). ^1H NMR (CD_2Cl_2): 7.45 (m, 2H, *o*-Ph), 7.36 (m, 1H, *p*-Ph), 7.27 (m, 2H, *p*-Ph), 4.94 (d, 1H, $^1J_{H-P}$ = 426 Hz, tBu$_3$P*H*), 1.60 (d, 27H,, $^3J_{H-P}$ = 16 Hz, t*Bu*$_3$PH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 150.45 (dm, $^1J_{C-F}$ = 230 Hz, *o*-C_6F_5), 140.71 (dm, $^1J_{C-F}$ = 246 Hz, *p*-C_6F_5), 136.86 (dm, $^1J_{C-F}$ = 246 Hz, *m*-C_6F_5), 131.80, 128.62, 128.19, 126.64, 38.18 (d, $^1J_{C-P}$ = 27 Hz, P*C*Me$_3$), 30.45 (s, PC*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −121.81 (s, br, 6F, *o*-C_6F_5), −158.576 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −164.44 (m, 6F, *m*-C_6F_5). ^{27}Al NMR (CD_2Cl_2): 105.18. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 61.76. Anal. Calcd for $C_{38}H_{33}F_{15}AlP$ (832.614): C, 54.82; H, 4.00. Found: C, 54.58; H, 4.18. X-ray quality crystals of **7**·(C_6H_5Cl) were grown by slow cooling of a solution in chlorobenzene.

8: colorless, crystalline solid, which was washed with pentane (2 × 5 mL) to afford a white solid (152 mg, 85%). ^1H NMR (CD_2Cl_2): 7.6 (d, 2H, $^3J_{H-H}$ = 7 Hz, *o*-B*Ph*), 7.4 (m, 2H, *o*-CCPh), 7.2 (tt, 2H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz, *m*-Ph),

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7.1 (m, 3H), 7.0 (tt, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz, *p*-Ph), 4.8 (d, 1H, $^1J_{H-P}$ = 430 Hz, *t*Bu$_3$P*H*), 1.5 (d, 27H, $^3J_{H-P}$ = 16 Hz, *tBu*$_3$PH). ^{11}B NMR (CD_2Cl_2): −17.1. $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 148.2 (dm, $^1J_{C-F}$ = 246 Hz, *o*-C_6F_5), 138.0 (dm, $^1J_{C-F}$ = 243 Hz, *p*-C_6F_5), 136.8 (dm, $^1J_{C-F}$ = 249 Hz, *m*-C_6F_5), 133.6, 131.5, 128.2, 126.5, 125.9, 123.9, 37.7 (d, $^1J_{C-P}$ = 26 Hz, P*C*Me$_3$), 30.1 (s, PC*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −130.9 (m, 6F, *o*-C_6F_5), −165.1 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.5 (m, 6F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 60.9. Anal. Calcd for $C_{38}H_{38}BF_{10}P$ (726.491): C, 62.83; H, 5.27. Found: C, 62.84; H, 5.49.

9: colorless, microcrystalline solid (263 mg, 49%). ^{1}H NMR (CD_2Cl_2): 7.5 (m, 8H, *o*-B*Ph* + *o*-CC*Ph*), 7.2 (tm, 2H, $^3J_{H-H}$ = 8 Hz, *m*-CC*Ph*), 7.1 (tm, 1H, $^3J_{H-H}$ = 7 Hz, *m*-CC*Ph*), 7.07 (t, 6H, $^3J_{H-H}$ = 7 Hz, *m*-B*Ph*), 6.9 (t, 3H, $^3J_{H-H}$ = 7 Hz, *p*-B*Ph*), 4.6 (d, 1H, $^1J_{H-P}$ = 436 Hz, *t*Bu$_3$P*H*), 1.4 (d, 27H, $^3J_{H-P}$ = 16 Hz, *tBu*$_3$PH). ^{11}B NMR (C_6D_5Br): −12.07. $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 134.7 (s), 131.1 (s), 127.9 (s), 126.1 (s), 125.0 (s), 122.6 (s), 37.2 (d, $^1J_{C\text{-}P}$ = 27 Hz, P*C*Me$_3$), 29.9 (s, PC*Me*$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 59.1 (s). Anal. Calcd for $C_{38}H_{48}BP$ (546.587): C, 83.50; H, 8.85. Found: C, 83.48; H, 9.20. X-ray quality crystals were grown by slow evaporation of a solution in CH_2Cl_2.

Synthesis of [*t*Bu$_3$PSiMe$_3$][Me$_3$SiCCB(C$_6$F$_5$)$_3$] (10). A solution of $B(C_6F_5)_3$ (104 mg, 0.2 mmol) in toluene (2 mL) was added in one portion to a solution of *t*Bu$_3$P (80 mg, 0.4 mmol) and $Me_3SiCCSiMe_3$ (100 mg, 0.6 mmol) in toluene (1 mL). The reaction mixture yellowed immediately, and during the course of 10 min the mixture became biphasic. Pentane (10 mL) was added and the bottom layer crystallized. The supernatant was decanted and the resulting white, microcrystalline solid dried *in vacuo* (81 mg, 45%). ^{1}H NMR (CD_2Cl_2): 1.6 (d, 27H, $^3J_{H-P}$ = 14 Hz, *tBu*$_3$PSiMe$_3$), 0.8 (d, 9H, $^3J_{H-P}$ = 5 Hz, *t*Bu$_3$PSi*Me*$_3$), 0.1 (s, 9H, CCSi*Me*$_3$). ^{11}B NMR (CD_2Cl_2): −21.4. $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 148.2 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 138.4 (dm, $^1J_{C-F}$ = 245 Hz, *p*-C_6F_5), 136.4 (dm, $^1J_{C-F}$ = 250 Hz, *m*-C_6F_5), 41.6 (d, $^1J_{C-P}$ = 18 Hz, P*C*Me$_3$), 31.4 (s, br, PC*Me*$_3$), 4.6 (d, $^2J_{C-P}$ = 4 Hz, PSi*Me*) 0.8 (s, Si*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −312.2 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −163.9 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −167.4 (t, 3F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 31.2 (s). Anal. Calcd for $C_{38}H_{45}BF_{15}Si_2P$ (884.710): C, 51.59; H, 5.13. Found: C, 51.07; H, 5.21. X-ray quality crystals were grown by slow cooling of the supernatant liquid; these crystals were weakly diffracting, connectivity was established, but the structure was not suitable for publication.

Synthesis of *E*-(*o*-tol)$_3$P(Ph)C═C(H)B(C$_6$F$_5$)$_3$ (11), *E*-Ph$_3$P-(R)C═C(H)B(C$_6$F$_5$)$_3$ (R = Ph (12), CpFe(C$_5$H$_4$) (13)), *E*-Ph$_3$P-(Ph)C═C(Me)B(C$_6$F$_5$)$_3$ (14), *E*-R$_2$PH(Ph)C═C(H)B(C$_6$F$_5$)$_3$ (R = Ph (15), C$_6$H$_2$Me$_3$ (16)), *E*-Ph$_3$P(Ph)C═C(H)BPh(C$_6$F$_5$)$_2$ (18), *E*-Ph$_3$P(Ph)C═C(H)Al(C$_6$F$_5$)$_3$ (19), *E*-Ph$_3$P(C$_4$H$_9$)C═C-(H)Al(C$_6$F$_5$)$_3$ (20), and *E*-(*o*-tol)$_3$P(Ph)C═C(H)Al(C$_6$F$_5$)$_3$ (21). These compounds were prepared in a similar fashion, and thus only one is detailed. PhCCH (0.3 mL, 23 mmol) was added in one portion to a slurry of $Ph_3P\cdot B(C_6F_5)_3$ (100 mg, 0.13 mmol) in chlorobenzene (3 mL). After 15 min of stirring the solution became clear and yellow and was stirred for an additional two hours, at which point the solvent was removed under reduced pressure and the resulting powder washed with a 10:1 mixture of pentane and chlorobenzene to afford an off-white powder (**12**).

11: 423 mg, 75%. ^{1}H NMR ($C_2D_2Cl_4$, 385 K): 8.18 (d, 1H, $^3J_{H-P}$ = 40 Hz, ═C-*H*), 7.85 (dd, 3H, J_{H-P} = 14 Hz, $^3J_{H-H}$ = 7 Hz), 7.67 (t, 3H, $^3J_{H-H}$ = 8 Hz), 7.49 (t, 2H, $^3J_{H-H}$ = 7 Hz), 7.33 (dd, 3H, J_{H-P} = 8 Hz, $^3J_{H-H}$ = 8 Hz), 7.08 (t, 1H, $^3J_{H-H}$ = 7 Hz, *p*-Ph), 6.93 (m, 4H, Ph), 1.80 (s, 9H, PC$_6$H$_4$*Me*). ^{11}B NMR ($C_2D_2Cl_4$, 385 K): −13.55 (d, $^3J_{B-P}$ = 16 Hz). ^{19}F NMR ($C_2D_2Cl_4$, 385 K): −128.83 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −160.14 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −164.34 (d, 6F, $^3J_{F-F}$ = 19 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR ($C_2D_2Cl_4$, 385 K): 31.09 (q, $^3J_{P-B}$ = 16 Hz). ^{1}H NMR (CD_2Cl_2, 215 K): (ratio of minor:major = 1:1.7) 8.49 (d, 1H, $^3J_{H-P}$ = 39 Hz, C═C-*H*, minor isomer), 8.41 (m, 1H, major isomer), 8.06 (dd, 1H, J_{H-P} = 12 Hz, $^3J_{H-H}$ = 8 Hz, minor isomer) 7.84 (d,1H, $^3J_{H-P}$ = 36 Hz, C═C-*H* major isomer), 7.78−6.33 (m, 16H of minor isomer, 14H of major isomer), 6.45 (d, $^3J_{H-H}$ = 8 Hz, major isomer), 2.55 (s, 3H, *o*-C$_6$H$_4$*Me* of minor isomer), 2.34 (s, 3H, *o*-C$_6$H$_4$*Me* of major isomer), 1.73 (s, 3H, *o*-C$_6$H$_4$*Me* of minor isomer), 1.68 (s, 3H, *o*-C$_6$H$_4$*Me* of minor isomer), 1.58 (s, 3H, *o*-C$_6$H$_4$*Me* of major isomer), 0.55 (s, 3H, *o*-C$_6$H$_4$*Me* of major isomer). ^{11}B NMR (CD_2Cl_2, 215 K): −15.35 (s), −15.75 (s). ^{19}F NMR (CD_2Cl_2, 215 K): −132.75 (s, br, *o*-C_6F_5), −161.60 (m, br, *p*-C_6F_5), −165.77 (s, br, *m*-C_6F_5), 166.23 (s, br, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 215 K): (ratio of minor:major 1:1.75) 30.52 (s, br, major), 27.05 (s, br, minor). $^{31}P\{^1H\}$ NMR (THF-d_8, 215 K): (ratio of minor: major 1:2.15) 30.80 (s, br, major), 27.41 (s, br, minor). Anal. Calcd for $C_{47}H_{27}BF_{15}P$ (918.495): C, 61.46; H, 2.96. Found: C, 61.89; H, 3.12. X-ray quality crystals of **11**·(C_6H_5Br) were grown by slow cooling of a solution in bromobenzene.

12: 98 mg, 87%. ^{1}H NMR (CD_2Cl_2): 8.3 (d, 1H, $^3J_{H-P}$ = 36 Hz, C═C-*H*), 7.8 (td, 3H, $^3J_{H-H}$ = 8 Hz, $^5J_{H\text{-}p}$ = 2 Hz, *p*-*Ph*P), 7.6 (td, 6H, $^3J_{H-H}$ = 8 Hz, $^4J_{H\text{-}p}$ = 6 Hz, *m*-*Ph*P), 7.4 (m, 6H, *o*-*Ph*P). ^{11}B NMR (CD_2Cl_2): −16.3 (d, $^3J_{B-P}$ = 14 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 148.1 (dm, $^1J_{C-F}$ = 236 Hz, *o*-C_6F_5), 138.4 (dm, $^1J_{C-F}$ = 242 Hz, *m*-C_6F_5), 136.5 (dm, $^1J_{C-F}$ = 246 Hz, *p*-C_6F_5), 134.6 (d, $^3J_{C-P}$ = 10 Hz, *m*-*Ph*P), 134.4 (d, $^4J_{C-P}$ = 3 Hz, *p*-*Ph*P), 129.6 (d, $^2J_{C-P}$ = 12 Hz, *o*-*Ph*P), 129.3 (d, $^3J_{C-P}$ = 5 Hz, *o*-*Ph*C), 127.9 (d, $^4J_{C-P}$ = 2 Hz, *m*-*Ph*C), 127.8 (d, $^5J_{C-P}$ = 2 Hz, *p*-*Ph*C), 119.5 (d, $^1J_{C-P}$ = 86 Hz, P-*C*═C). ^{19}F NMR (C_6D_5Br): −130.6 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −160.8 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −165.1 (d, 6F, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 25.2 (q, $^3J_{P-B}$ = 15 Hz). Anal. Calcd for $C_{47}H_{27}BF_{15}P$ (876.414): C, 60.30; H, 2.42. Found: C, 60.65; H, 2.72. X-ray quality crystals were grown by slow evaporation of a solution in CH_2Cl_2.

13: 120 mg, 58%. ^{1}H NMR (CD_2Cl_2): 8.0 (d, 1H, $^3J_{H-P}$ = 39 Hz, C═C-*H*), 7.9−7.8 (m, 9H), 7.7 (td, 6H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 3 Hz, *m*-*Ph*), 3.9 (m, 2H, *Cp*′), 3.5 (m, 2H, *Cp*′), 3.4 (s, 5H, *Cp*). ^{11}B NMR (CD_2Cl_2): −16.3 (d, $^1J_{B-P}$ = 16 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 192.8 (m, C═*C*-B), 148.7 (dm, $^1J_{C-F}$ = 232 Hz, *o*-C_6F_5), 139.0 (dm, $^1J_{C-F}$ = 240 Hz, *p*-C_6F_5), 137.3 (dm, $^1J_{C-F}$ = 242 Hz, *m*-C_6F_5), 135.2 (d, J_{C-P} = 8 Hz), 134.8 (d, J_{C-P} = 3 Hz), 130.2 (d, J_{C-P} = 12 Hz), 121.6 (d, J_{C-P} = 88 Hz), 118.6 (d, J_{C-P} = 78 Hz), 84.4 (d, J_{C-P} = 15 Hz, *1-Cp*′), 71.1 (d, J_{C-P} = 5 Hz, *2-Cp*′), 69.8 (s, *Cp*), 68.1 (s, *3-Cp*′). ^{19}F NMR (CD_2Cl_2): −131.7 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −162.9 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.2 (d, 6F, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 23.4 (d, $^1J_{P-B}$ = 16 Hz). Anal. Calcd for $C_{48}H_{25}BF_{15}PFe\cdot CH_2Cl_2$ (984.335): C, 55.04; H, 2.45. Found: C, 55.30; H, 2.89. X-ray quality crystals were grown by slow cooling of a solution in CH_2Cl_2.

14: colorless crystals (88 mg, 77%). ^{1}H NMR (373 K, $C_2D_2Cl_4$): 7.7 (m, 3H, *p*-P*Ph*), 7.7−7.5 (m, 12H, P*Ph*), 6.9−6.7 (m, 5H, *Ph*C═C), 1.9 (s, br, 3H, C═C*Me*). ^{11}B NMR (293 K, CD_2Cl_2): −13.0 (s, br). ^{19}F NMR (293 K, CD_2Cl_2): −122.7 (s, br, 1F, *o*-C_6F_5), −128.7 (s, br, 1F, *o*-C_6F_5), −130.1 (s, br, 1F, *o*-C_6F_5), −130.8 (s, br, 1F, *o*-C_6F_5), −132.4 (d, 1F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −132.7 (s, br, 1F, *o*-C_6F_5), −162.2 (t, br, 1F, $^3J_{F-F}$ = 23 Hz, *p*-C_6F_5), −162.3 (t, 1F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −163.0 (t, br, 1F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.4 to −166.9 (m, 4F, *m*-C_6F_5), −167.1 (t, br, 1F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5), −167.5 (t, br, 1F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (293 K, CD_2Cl_2): 16.5 (q, $^3J_{P-B}$ = 16 Hz). Anal. Calcd for $C_{45}H_{23}BF_{15}P$ (890.441): C, 60.70; H, 2.60. Found: C, 60.59; H, 2.94.

15: white, microcrystalline solid, 163 mg, 70%. ^{1}H NMR (CD_2Cl_2): 8.3 (d, 1H, $^3J_{H-P}$ = 39 Hz, C═C-*H*), 7.9 (d, 1H, $^1J_{H-P}$ = 225 Hz, Ph$_2$P*H*), 7.8 (m, 2H), 7.7−7.6 (m, 8H), 7.1 (tm, 1H, $^3J_{H-H}$ = 7 Hz, *p*-CCPh), 7.0 (t, 2H, $^3J_{H-H}$ = 7 Hz, *m*-CCPh), 6.8 (dm, 2H, $^3J_{H-H}$ = 7 Hz, *o*-CCPh). ^{11}B NMR (CD_2Cl_2): −16.1 (d, $^1J_{B-P}$ = 18 Hz). $^{13}C\{^1H\}$ NMR (139.06 CD_2Cl_2), partial: 148.3 (dm, $^1J_{C-F}$ = 248 Hz, *o*-C_6F_5), 135.7 (d, J_{C-P} = 4 Hz), 134.2 (d, J_{C-P} = 10 Hz), 130.7 (d, J_{C-P} = 12 Hz), 128.8 (d, J_{C-P} = 6 Hz), 128.6 (d, J_{C-P} = 3 Hz), 128.5 (d, J_{C-P} = 3 Hz). ^{19}F NMR (CD_2Cl_2): −132.0 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −162.4 (t, 3F,

$^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −166.8 (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 14.4 (d, $^1J_{P-B}$ = 18 Hz). Anal. Calcd for $C_{38}H_{17}BF_{15}P$ (800.316): C, 57.03; H, 2.14. Found: C, 57.56; H, 2.56. X-ray quality crystals were grown by layering a solution in CH_2Cl_2 with pentane.

16: white solid, 215 mg, 78%. ^1H NMR (CD_2Cl_2): 8.0 (d, 1H, $^1J_{H-P}$ = 461 Hz, P*H*), 7.9 (d, 1H, $^3J_{H-P}$ = 42 Hz, C═C-*H*), 7.1−7.0 (m, 5H), 7.0 (d, 4H, J_{H-H} = 5 Hz), 2.4 (s, 12H, *p*-*Me*), 2.3 (s, 6H, *o*-*Me*). ^{11}B NMR (CD_2Cl_2): −15.6 (d, $^3J_{B-P}$ = 18 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 181.0 (m, C═*C*-B), 147.9 (dm, $^1J_{C-F}$ = 236 Hz, *o*-C_6F_5), 145.8 (d, J_{C-P} = 3 Hz), 143.8 (d, J_{C-P} = 10 Hz), 138.4 (dm, $^1J_{C-F}$ = 250 Hz, *p*-C_6F_5), 136.5 (dm, $^1J_{C-F}$ = 242 Hz, *m*-C_6F_5), 131.4 (d, J_{C-P} = 11 Hz), 128.4 (d, J_{C-P} = 7 Hz), 128.2 (d, J_{C-P} = 3 Hz), 127.8 (d, J_{C-P} = 10 Hz), 112.9, 112.2, 21.3 (d, $^5J_{C-P}$ = 8 Hz, *o*-*C*H_3), 20.9 (s, *p*-*C*H_3). ^{19}F NMR (CD_2Cl_2): −132.4 (d, 6F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −162.5 (t, 3F, $^3J_{F-F}$ = 19 Hz, *p*-C_6F_5), −166.8 (d, 6F, $^3J_{F-F}$ = 24 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 12.9 (q, $^3J_{P-B}$ = 18 Hz). Anal. Calcd for $C_{44}H_{29}BF_{15}P$ (884.478): C, 59.75; H, 3.30. Found: C, 59.80; H, 3.09. X-ray quality crystals were grown by slow cooling of a solution in CH_2Cl_2.

18: white, microcrystalline solid, 220 mg, 92%. ^1H NMR (CD_2Cl_2): 8.3 (d, 1H, $^3J_{H-P}$ = 36 Hz, C═C-*H*), 7.7 (tm, 3H, $^3J_{H-H}$ = 8 Hz), 7.5 (tm, 6H, $^3J_{H-H}$ = 8 Hz), 7.4−7.3 (m, 6H), 7.3 (d, br, 2H, $^3J_{H-H}$ = 7 Hz), 7.2−7.0 (m, 4H), 6.9 (t, 2H, $^3J_{H-H}$ = 8 Hz), 6.8 (d, 2H, $^3J_{H-H}$ = 7 Hz). ^{11}B NMR (CD_2Cl_2): −12.6 (s, br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 186.2 (m, C═*C*-B), 147.6 (dm, $^1J_{C-F}$ = 237 Hz, *o*-C_6F_5), 138.0 (dm, $^1J_{C-F}$ = 244 Hz, *p*-C_6F_5), 136.5 (dm, $^1J_{C-F}$ = 248 Hz, *m*-C_6F_5), 131.8 (d, J_{C-P} = 17 Hz), 134.5 (d, J_{C-P} = 9 Hz), 134.2 (s), 133.2 (s), 130.1 (d, J_{C-P} = 6 Hz), 129.5 (d, J_{C-P} = 13 Hz), 127.7(s), 127.6 (s), 126.6 (s), 124.0 (s), 120.5 (s), 119.7 (s), 117.4 (d, $^1J_{C-P}$ = 86 Hz, P-*C*═C). ^{19}F NMR (CD_2Cl_2): −128.8 (d, 4F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −163.5 (t, 2F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −166.7 (d, 4F, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 24.9 (s, br). Anal. Calcd for $C_{50}H_{30}BF_{15}P_2$ (988.526): C, 60.75; H, 3.06. Found: C, 61.09; H 3.16. X-ray quality crystals were grown by layering a solution in CH_2Cl_2 with pentane.

19: ^1H NMR (CD_2Cl_2): 8.2 (d, 1H, $^3J_{H-P}$ = 39 Hz, C═C-*H*), 7.8 (tm, 3H, $^3J_{H-H}$ = 7 Hz, *p*-PPh), 7.6 (td, 6H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 4 Hz, *m*-PPh), 7.4 (dd, 6H, $^3J_{H-P}$ = 12 Hz, $^3J_{H-H}$ = 7 Hz, *o*-PPh), 7.08 (tm, 1H, $^3J_{H-H}$ = 7 Hz, *p*-Ph), 6.9 (t, 2H, $^3J_{H-H}$ = 7 Hz, *m*-Ph), 6.7 (d, 6H, $^3J_{H-H}$ = 7 Hz, *o*-Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 149.5 (dm, $^1J_{C-F}$ = 231 Hz, *o*-C_6F_5), 140.2 (dm, $^1J_{C-F}$ = 244 Hz, *p*-C_6F_5), 136.1 (dm, $^1J_{C-F}$ = 255 Hz, *m*-C_6F_5), 134.6 (s), 134.5 (s), 134.4 (s), 129.7 (d, J_{C-P} = 13 Hz), 129.5 (d, J_{C-P} = 5 Hz), 128.1 (d, J_{C-P} = 13 Hz), 127.7 (d, J_{C-P} = 2 Hz), 119.3 (d, J_{C-P} = 85 Hz). ^{19}F NMR (CD_2Cl_2): −121.8 (d, 6F, $^3J_{F-F}$ = 20 Hz, *o*-C_6F_5), −157.9 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −164.2 (m, 6F, *m*-C_6F_5). ^{27}Al NMR (CD_2Cl_2): 115.0 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 23.4 (s, br). Anal. Calcd for $C_{44}H_{21}F_{15}AlP$ (892.584): C, 59.21; H, 2.37. Found: C, 59.68; H, 2.51. X-ray quality crystals were grown from layering a solution in CH_2Cl_2 with pentane.

20: colorless crystals, 112 mg, 42%. ^1H NMR (CD_2Cl_2): 7.9−7.8 (m, 3H), 7.8 (d, $^3J_{H-H}$ = 41 Hz P-C═C(*H*)-Al), 7.7−7.6 (m, 12 H), 2.4 (m, 2H, C═C-CH_2), 0.8−0.7 (m, 4H, $CH_2CH_2CH_3$), 0.5 (t, 3H, $^3J_{H-H}$ = 7 Hz, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 181 (m, br, C═*C*-Al), 150.4 (dm, $^1J_{C-F}$ = 231 Hz, *o*-C_6F_5), 141.0 (dm, $^1J_{C-F}$ = 240 Hz, *p*-C_6F_5), 137.0 (dm, $^1J_{C-F}$ = 251 Hz, *m*-C_6F_5), 135.1 (d, J_{C-P} = 3 Hz), 134.8 (d, J_{C-P} = 10 Hz), 132.4 (d, J_{C-P} = 47 Hz), 130.5 (d, J_{C-P} = 14 Hz), 120.6 (d, J_{C-P} = 87 Hz), 36.2 (d, J_{C-P} = 21 Hz), 33.1 (s), 22.9 (s), 13.5 (s). ^{19}F NMR (CD_2Cl_2): −121.9 (d, 6F, $^3J_{F-F}$ = 20 Hz, *o*-C_6F_5), −157.3 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −163.8 (m, 6F, *m*-C_6F_5). ^{27}Al NMR (CD_2Cl_2): 114.7 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 23.0 (s, br). Anal. Calcd for $C_{42}H_{25}F_{15}AlP$ (892.584): C, 57.81; H, 2.89. Found: C, 57.59; H 3.27. The product crystals were suitable for X-ray diffraction.

21: 73 mg, 84%. ^1H NMR ($C_2D_2Cl_4$, 385 K): 8.05 (d, 1H, $^3J_{H-P}$ = 43 Hz, ═C-*H*), 7.79 (s, br, 3H), 7.70 (t, 3H, $^3J_{H-H}$ = 8 Hz), 7.51 (t, 2H, $^3J_{H-H}$ = 7 Hz), 7.38 (dd, 3H, J_{H-P} = 7 Hz, $^3J_{H-H}$ = 7 Hz), 7.10 (t, 1H, $^3J_{H-H}$ = 7 Hz, *p*-Ph), 6.98 (m, 4H, Ph), 1.88 (s, 9H, PC_6H_4Me). ^{19}F NMR ($C_2D_2Cl_4$, 385 K): −119.35 (s, br, 6F, *o*-C_6F_5), −155.63 (t, 3F, $^3J_{F-F}$ = 19 Hz, *p*-C_6F_5), −161.93 (m, 6F, *m*-C_6F_5). ^{27}Al NMR ($C_2D_2Cl_4$, 385 K): 116.52 (s, br). $^{31}P\{^1H\}$ NMR ($C_2D_2Cl_4$, 385 K): 26.13 (s, br). Anal. Calcd for $C_{47}H_{27}F_{15}AlP$ (934.665): C, 60.40; H, 2.91. Found: C, 59.93; H, 3.38. X-ray quality crystals of **21**·(CH_2Cl_2) were grown by slow evaporation of a solution in CH_2Cl_2.

Synthesis of *E*-($C_6H_2tBu_3$)PH_2(Ph)C═C(H)B(C_6F_5)$_3$ (17). To a solution of (2,4,6-$C_6H_2tBu_3$)PH_2 (43 mg, 0.15 mmol) and B(C_6F_5)$_3$ (79 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was added in one portion PhCCH (0.2 mL, 2.1 mmol). The reaction mixture went from colorless to a light peach upon this addition. The solution was layered with pentane (5 mL) and cooled to −35 °C overnight, affording clear, colorless crystals (120 mg, 90%). ^1H NMR (CD_2Cl_2): 8.1 (s, 1H, C═C-*H*), 7.8 (d, 2H, $^4J_{H-P}$ = 4 Hz, *m*-C_{Ar}-*H*), 7.4−7.2 (m, 4H), 7.0−6.9 (m, 3H), 1.5 (s, *o*-*t*Bu), 1.4 (s, *p*-*t*Bu). ^{11}B NMR (CD_2Cl_2): −16.3 (d, $^1J_{B-P}$ = 16 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 181.3 (q, $^1J_{C-B}$ = 45 Hz, C═*C*-B), 159.8 (d, J_{C-P} = 2 Hz), 159.2 (d, J_{C-P} = 2 Hz), 148.4 (dm, $^1J_{C-F}$ = 238 Hz, *o*-C_6F_5), 139.0 (dm, $^1J_{C-F}$ = 250 Hz, *p*-C_6F_5), 136.9 (dm, $^1J_{C-F}$ = 248 Hz, *m*-C_6F_5), 135.9 (d, J_{C-P} = 19 Hz), 129.3 (d, J_{C-P} = 3 Hz), 129.2 (d, J_{C-P} = 1 Hz), 128.5 (d, J_{C-P} = 6 Hz), 125.7 (d, J_{C-P} = 13 Hz), 119.3 (d, J_{C-P} = 65 Hz), 102.2 (d, J_{C-P} = 76 Hz), 38.9 (d, J_{C-P} = 4 Hz, *o*-*C*Me_3), 36.4 (s, *p*-*C*Me_3), 34.1 (s, *o*-C*Me*$_3$), 30.9 (s, *p*-C*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −131.6 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −162.4 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −166.8 (d, 6F, $^3J_{F-F}$ = 22 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −31.1 (q, $^3J_{P-B}$ = 17 Hz). Anal. Calcd for $C_{44}H_{37}BF_{15}P$ (892.542): C, 59.21; H, 4.18. Found: C, 59.13; H, 4.60. The crystalline product was suitable for X-ray diffraction.

Synthesis of [(H)C═C(Ph)$Mes_2PC_6F_4B(C_6F_5)_2]_2$ (22) and *E*-$Ph_2PCH_2CH_2PPh_2$(Ph)C═C(H)B(C_6F_5)$_3$ (23). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. To a solution of $Mes_2P-C_6F_4-B(C_6F_5)_2$ (35 mg, 0.05 mmol) in toluene (3 mL) was added in one portion PhCCH (0.1 mL, 0.9 mmol). After 30 min pentane (15 mL) was added to precipitate an off-white powder, which was dried *in vacuo*.

22: 30 mg, 81%. ^1H NMR (CD_2Cl_2): 8.7 (m, br, P-C═C(*H*)-B), 7.3 (m, br, 2H), 7.0 (m, br, 3H), 6.7 (s, br, 2H), 2.2 (s, br, 3H), 2.0 (m, br, 3H), 1.9 (m, br, 3H). ^{11}B NMR (CD_2Cl_2): −13.2 (s, br). ^{19}F NMR (CD_2Cl_2): −129 0.4 (s, br, 2F, C_6F_4), −130.6 (m, br, 2F, C_6F_4), −134.1 (s, br, 2F, C_6F_4), −135.5 (m, 4F, *o*-C_6F_5), −136.0 (m, 4F, *o*-C_6F_5), −137.0 (m, br, 2F, C_6F_4), −159.3 (s, br, 2F, *p*-C_6F_5), −159.7 (s, br, 2F, *p*-C_6F_5), −165.0 to −165.5 (m, 8F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −37.2 (m, br). Anal. Calcd for $C_{72}H_{56}B_2F_{28}P_2$ (1536.766): C, 56.27; H, 3.67. Found: C, 56.26; H, 3.26. X-ray quality crystals were grown from slow evaporation of a solution in toluene/CH_2Cl_2.

23: white microcrystalline solid: 163 mg, 56%. ^1H NMR (CD_2Cl_2): 8.34 (d, 1H, $^3J_{H-P}$ = 35 Hz, C═C-*H*), 7.8 (tm, 2H, $^3J_{H-H}$ = 8 Hz), 7.6 (tm, 4H, $^3J_{H-H}$ = 8 Hz), 7.6−7.5 (m, 4H), 7.4−7.3 (m, 6H), 7.2−7.1 (m, 4H), 7.1 (tm, 1H, $^3J_{H-H}$ = 8 Hz), 6.9 (t, 2H, $^3J_{H-H}$ = 7 Hz), 6.5 (d, 2H, $^3J_{H-H}$ = 8 Hz), 2.3 (m, 2H, $R_2PCH_2CH_2PR_3$), 2.0 (m, 2H, $R_2PCH_2CH_2PR_3$). ^{11}B NMR (CD_2Cl_2): −16.3 (d, $^3J_{B-P}$ = 14 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 148.5 (dm, $^1J_{C-F}$ = 249 Hz, *o*-C_6F_5), 138.7 (dm, $^1J_{C-F}$ = 245 Hz, *p*-C_6F_5), 136.9 (dm, $^1J_{C-F}$ = 244 Hz, *m*-C_6F_5), 136.5 (d, J_{C-P} = 12 Hz), 135.0 (d, J_{C-P} = 3 Hz), 133.9 (d, J_{C-P} = 9 Hz), 132.9 (d, J_{C-P} = 18 Hz), 130.4 (d, J_{C-P} = 12 Hz), 129.8, 129.3, 129.2, 128.8 (d, J_{C-P} = 5 Hz), 128.5 (d, J_{C-P} = 5 Hz), 128.3 (d, J_{C-P} = 3 Hz), 120.2, 20.4 (dd, $^1J_{C-P}$ = 51 Hz, $^3J_{C-P}$ = 27 Hz), 19.9 (dd, $^1J_{C-P}$ = 18 Hz, $^3J_{C-P}$ = 6 Hz). ^{19}F NMR (CD_2Cl_2): −131.7 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −162.6 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.8 (d, 6F, $^3J_{F-F}$ = 22 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 24.97 (m, *P*-C═C-B) −10.5 (d, $^3J_{P-P}$ = 45 Hz, $-CH_2PPh_2$). Anal. Calcd for $C_{50}H_{30}BF_{15}P_2$ (988.526): C, 60.75; H, 3.06. Found: C, 61.09; H, 3.16.

Synthesis of *E*-(CH_2PPh_2(Ph)C=C(H)B(C_6F_5)$_3$)$_2$ (24). PhCCH (0.1 mL, 0.9 mmol) was added in one portion to a slurry of (CH_2PPh_2)$_2$ (50 mg, 0.125 mmol) and B(C_6F_5)$_3$ (128.5 mg, 0.25 mmol) in CH_2Cl_2 (5 mL). The solution was stirred for ~2 h, resulting in a white precipitate. The supernatant solvent was decanted and the powder dried under reduced pressure (180 mg, 89%). The product was not sufficiently soluble in a variety of deuterated solvents (d_8-THF, CD_2Cl_2, C_6D_5Br) to allow for characterization by NMR spectroscopy. Anal. Calcd for $C_{78}H_{36}B_2F_{30}P_2 \cdot CH_2Cl_2$ (1711.602): C, 55.44; H, 2.24. Found: C, 55.95; H, 2.42. X-ray quality crystals were grown from the undisturbed supernatant solution in CH_2Cl_2.

Synthesis of *E*-HC≡CC_6H_4C(PPh_3)=C(H)B(C_6F_5)$_3$ (25). To a slurry of $Ph_3P \cdot B(C_6F_5)_3$ (151 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was added in one portion 1,4-diethynylbenzene (26 mg, 0.2 mmol). The reaction mixture yellowed slightly and was then stirred overnight, after which point the $Ph_3P \cdot B(C_6F_5)_3$ had dissolved completely. The volume was reduced to half the original volume *in vacuo*, layered with pentane (5 mL), and cooled to −35 °C overnight to afford colorless crystals (170 mg, 97%). ^{1}H NMR (CD_2Cl_2): 8.4 (d, 1H, $^3J_{H-P}$ = 35 Hz, C=C-*H*), 7.8 (td, 3H, $^3J_{H-H}$ = 7 Hz, $^5J_{H-P}$ = 2 Hz, *p*-*Ph*P), 7.6 (td, 6H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 4 Hz, *m*-*Ph*P), 7.5 (m, 6H), 7.1 (d, 2H, $^3J_{H-H}$ = 8 Hz), 6.5 (dd, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-p}$ = 2 Hz), 3.2 (s, 1H, CC*H*). ^{11}B NMR (CD_2Cl_2): −16.3 (d, $^3J_{B-P}$ = 14 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 183.6 (q, $^1J_{C-B}$ = 50 Hz, C=*C*-B) 148.0 (dm, $^1J_{C-F}$ = 237 Hz, *o*-C_6F_5), 138.5 (dm, $^1J_{C-F}$ = 244 Hz, *m*-C_6F_5), 136.5 (dm, $^1J_{C-F}$ = 255 Hz, *p*-C_6F_5), 135.6 (d, J_{C-P} = 15 Hz), 134.5 (s), 134.5 (s), 131.9 (s), 131.5 (d, J_{C-P} = 3 Hz), 129.8 (d, J_{C-P} = 13 Hz), 129.3 (d, $^3J_{C-P}$ = 6 Hz), 123.0 (s), 122.5 (s), 121.8 (d, J_{C-P} = 3 Hz), 119.5 (s), 118.7 (s), 82.0 (s, *C*CH), 78.0 (s, C*C*H). ^{19}F NMR (CD_2Cl_2): −131.6 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −162.5 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.8 (d, 6F, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 25.2 (q, $^3J_{P-B}$ = 14 Hz). Anal. Calcd for $C_{46}H_{21}BF_{15}P$ (900.436): C, 61.36; H, 2.35. Found: C, 61.44; H, 2.62. X-ray quality crystals were grown by slow cooling of a solution in CH_2Cl_2.

Synthesis of [*t*Bu_3PH][(C_6F_5)$_3$BCCC_6H_4C(PPh_3)=C(H)B(C_6F_5)$_3$] (26). CH_2Cl_2 (3 mL) was added to an intimate mixture of **25** (100 mg, 0.1 mmol), *t*Bu_3P (40 mg, 0.2 mmol), and B(C_6F_5)$_3$ (57 mg, 0.1 mmol). After dissolution the reaction mixture was immediately layered with pentane (15 mL). After ~16 h, off-white crystals formed and were subsequently dried under reduced pressure (148 mg, 83%). ^{1}H NMR (CD_2Cl_2): 8.3 (d, 1H, $^3J_{H-P}$ = 36 Hz, C=C-*H*), 7.8 (tm, 3H, $^3J_{H-H}$ = 7 Hz, *p*-*Ph*P), 7.6 (td, 6H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 3 Hz, *m*-*Ph*P), 7.4 (dd, 6H, $^3J_{H-P}$ = 13 Hz, $^3J_{H-H}$ = 8 Hz, *o*-*Ph*P), 6.8 (d, 2H, $^3J_{H-H}$ = 8 Hz, −C_6H_4−), 6.3 (dd, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 2 Hz, −C_6H_4−), 5.0 (d, 1H, $^1J_{H-P}$ = 428 Hz), 1.6 (d, 27H, $^3J_{H-P}$ = 16 Hz, *t*Bu_3PH). ^{11}B NMR (CD_2Cl_2): −16.3 (s, br, P-C=C-*B*), −20.9 (s, CC-*B*). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 183.6 (m, C=*C*-B), 148.8 (dm, $^1J_{C-F}$ = 235 Hz, *o*-C_6F_5), 138.9 (dm, $^1J_{C-F}$ = 255 Hz, *m*-C_6F_5), 137.0 (dm, $^1J_{C-F}$ = 248 Hz, *p*-C_6F_5), 135.2 (d, J_{C-P} = 10 Hz), 135.0 (d, J_{C-P} = 3 Hz), 132.5 (d, J_{C-P} = 13 Hz), 131.1 (s), 130.3 (d,, J_{C-P} = 13 Hz), 129.4 (d, J_{C-P} = 4 Hz), 128.1 (s, br), 124.9 (s, br), 124 (s, br), 120.6 (s), 119.4 (s), 38.2 (d, $^1J_{C-P}$ = 30 Hz, PCMe_3), 30.5 (s, PCMe_3). ^{19}F NMR (CD_2Cl_2): −131.5 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −132.6 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −162.7 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −163.9 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.7 (d, 6F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5), −167.4 (d, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 61.7 (s, *t*Bu_3*P*H), 24.7 (m, *P*-C=C-B). Anal. Calcd for $C_{76}H_{48}B_2F_{30}P_2$ (1614.743): C, 56.53; H, 3.00. Found: C, 56.93; H, 3.27.

Synthesis of [$PhCH_2NMe_2H$][PhCCB(C_6F_5)$_3$] (27a). A solution of B(C_6F_5)$_3$ (100 mg, 0.2 mmol) in CH_2Cl_2 (3 mL) was added to a mixture of $PhCH_2NMe_2$ (27 mg, 0.2 mmol) and PhCCH (20 mg, 0.2 mmol) in CH_2Cl_2 (3 mL) in one portion. The solvent was removed under reduced pressure, and the white residue washed with pentane (5 mL) and dried *in vacuo* to afford a white solid (136 mg, 94%). NMR spectroscopy revealed this solid to be the isomers resulting from deprotonation (**27a**, 84% by ^{19}F NMR) and addition (**27b**, 16%). Recrystallization from bromobenzene afforded only the isomer formed from deprotonation as colorless crystals (82 mg, 57%). ^{1}H NMR (CD_2Cl_2): 7.6 (tt, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz), 7.5 (tm, 2H, $^3J_{H-H}$ = 7 H, *m*-Ph), 7.4−7.3 (m, 2H), 7.3−7.2 (m, 5H) 6.40 (s, br, 1H, N*H*), 4.0 (s, 2H, NCH_2Ph), 2.6 (s, 6H, N(CH_3)$_2$), 1.29 (s, 12H, *Me*). ^{11}B NMR (CD_2Cl_2): −20.8. ^{13}C{^{1}H} NMR (CD_2Cl_2), partial: 148.0 (dm, $^1J_{C-F}$ = 250 Hz, *o*-C_6F_5), 138.5 (dm, $^1J_{C-F}$ = 236 Hz, *p*-C_6F_5), 136.7 (dm, $^1J_{C-F}$ = 250 Hz, *m*-C_6F_5), 131.4 (s), 131.3 (s), 130.6 (s), 129.9 (s), 128.8 (s), 127.4 (s), 126.2 (s), 125.8 (s), 63.2 (s, NCH_2Ph), 43.6 (s, N(CH_3)$_2$). ^{19}F NMR (CD_2Cl_2): −133.2 (d, 6F, $^3J_{F-F}$ = 25 Hz, *o*-C_6F_5), −162.3 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.4 (t, 6F, $^3J_{F-F}$ = 22 Hz, *m*-C_6F_5). Anal. Calcd for $C_{35}H_{19}BNF_{15}$ (749.332): C, 56.10; H, 2.56; N, 1.87. Found: C, 55.96; H, 2.67; N, 2.03.

Synthesis of [(*t*Bu)HN=C(R)Ph][PhCCB(C_6F_5)$_3$] (R = H (28), Ph (29)). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. A solution of B(C_6F_5)$_3$ (42 mg, 0.08 mmol) in toluene (3 mL) was added dropwise to a solution of *tert*-butylbenzylideneimine (14 mg, 0.09 mmol) and PhCCH (0.1 mL, 1.1 mmol) in toluene (4 mL) at room temperature. The reaction mixture turned bright yellow and was left undisturbed for 2 days, affording large colorless crystals of **28** with cocrystallized toluene (52 mg, 73%). ^{1}H NMR (CD_2Cl_2): 9.7 (s, br, 1H, C=N*H*), 8.4 (s, 1H, C(*H*)=N), 8.0 (dm, 2H, $^3J_{H-H}$ = 8 Hz), 7.9 (tm, 1H, $^3J_{H-H}$ = 7 Hz), 7.7 (tm, 2H, $^3J_{H-H}$ = 8 Hz), 7.2 (m, 2H), 7.1 (m, 3H), 1.5 (s, 9H, *tBu*). ^{11}B NMR (CD_2Cl_2): −20.8 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2), partial: 167.9 (s, *C*=N), 148.8 (dm, $^1J_{C-F}$ = 235 Hz), 140.3 (s), 138.8 (dm, $^1J_{C-F}$ = 245 Hz), 133.2 (dm, $^1J_{C-F}$ = 250 Hz), 132.5 (s), 131.6 (s), 131.2 (s), 129.6 (s), 128.8 (s), 128.7 (s), 127.2 (s), 127.1 (s), 125.8 (s), 125.6 (s), 63.7 (s, *C*Me$_3$), 28.5 (s, C*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −132.6 (d, 6F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −163.1 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −166.8 (d, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{37}H_{21}BNF_{15} \cdot C_7H_8$ (867.510): C, 60.92; H, 3.37; N, 1.61. Found: C, 60.70; H, 3.32; N, 1.65.

29: light yellow, crystalline solid (54 mg, 73%). ^{1}H NMR ($C_2D_2Cl_4$): 9.1 (s, br, 1H, N*H*), 7.9 (t, 1H, $^3J_{H-H}$ = 8 Hz), 7.8 (t, 2H, $^3J_{H-H}$ = 8 Hz), 7.7 (t, 2H, $^3J_{H-H}$ = 8 Hz), 7.6 (t, 2H, $^3J_{H-H}$ = 8 Hz), 7.4 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.3 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.3 (m, 2H), 7.2 (m, 3H), 1.4 (s, 9H, *tBu*). ^{11}B NMR ($C_2D_2Cl_4$): −20.8 (s). ^{13}C{^{1}H} NMR ($C_2D_2Cl_4$), partial: 183.8 (s, N=*C*), 148.1 (dm, $^1J_{C-F}$ = 242 Hz, *o*-C_6F_5), 138.1 (s), 137.4 (dm, $^1J_{C-F}$ = 245 Hz, *p*-C_6F_5), 136.3 (dm, $^1J_{C-F}$ = 242 Hz, *m*-C_6F_5), 134.4 (s), 132.2 (s), 131.3 (s), 130.25 (s), 129.7 (s), 129.1 (s), 128.9 (s), 128.7 (s), 127.9 (s), 126.9 (s), 126.1 (s), 64.7 (s, *C*Me$_3$), 28.3 (s, C*Me*$_3$). ^{19}F NMR ($C_2D_2Cl_4$): −134.7 (d, 6F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −162.1 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −165.8 (d, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{43}H_{25}BNF_{15}$ (851.467): C, 60.66; H, 2.96; N, 1.65. Found: C, 60.57; H, 2.71; N, 1.66. X-ray quality crystals were grown by slow cooling of a solution in bromobenzene.

Synthesis of [*t*BuNCN(H)C(Ph)=C(H)*t*Bu][PhCCB(C_6F_5)$_3$] (30). A solution of PhCCH (40 mg, 0.39 mmol) in CH_2Cl_2 (1 mL) was added in one portion to a solution of *t*BuNCN*t*Bu (28 mg, 0.2 mmol) and B(C_6F_5)$_3$ (120 mg, 0.23 mmol) in CH_2Cl_2 (3 mL). The reaction became bright red after the addition. The solvent was removed under reduced pressure, and the resulting solid dissolved in chlorobenzene (1 mL) and layered with pentane (4 mL). The layered mixture was cooled to −35 °C overnight to afford colorless crystals (108 mg, 64%). ^{1}H NMR (CD_2Cl_2): 7.6 (tt, 1H, $^3J_{H-H}$ = 7 Hz, $^5J_{H-H}$ = 1 Hz, *p*-Ph), 7.5 (tm, 2H, $^3J_{H-H}$ = 7 Hz, *m*-Ph), 7.4 (dm, 2H, $^3J_{H-H}$ = 7 Hz, *o*-Ph), 7.3 (m, 3H), 7.19 (t, 2H, $^3J_{H-H}$ = 7 Hz), 7.1 (m, 1H), 6.0 (s, br, 1H, N*H*), 4.69 (s, 1H, C=C*H*), 1.45 (s, 9H, *tBu*), 1.29 (s, 9H, *tBu*). ^{11}B NMR (CD_2Cl_2): −20.9. ^{13}C{^{1}H} NMR (CD_2Cl_2), partial: 172.3 (s, N*C*N), 148.3 (dm, $^1J_{C-F}$ = 231 Hz, *o*-C_6F_5), 138.3 (dm, $^1J_{C-F}$ = 243 Hz, *p*-C_6F_5), 136.5 (dm, $^1J_{C-F}$ = 248 Hz, *m*-C_6F_5), 134.6, 134.1, 132.8, 131.1, 129.8, 129.7, 128.5, 127.8, 127.5,

127.3, 126.4, 125.7, 63.1 (s, *C*Me$_3$), 56.0 (s, *C*Me$_3$), 29.0 (s, C*Me*$_3$), 28.0 (s, C*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −132.6 (d, 6F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −163.8 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −167.3 (t, 6F, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5). Anal. Calcd for $C_{43}H_{32}BN_2F_{15}$ (872.530): C, 59.19; H, 3.70; N, 3.21. Found: C 59.80; H, 3.58; N, 3.28. X-ray quality crystals were grown by slow cooling of a solution in chlorobenzene.

Synthesis of [I*t*BuH][PhCCB(C_6F_5)$_3$] (31). A solution of PhCCH (40 mg, 0.4 mmol) and 1,3-di-*tert*-butylimidazol-2-ylidene (I*t*Bu) (54 mg, 0.3 mmol) in toluene (5 mL) was cooled to −78 °C, at which point B(C_6F_5)$_3$ (153 mg, 0.3 mmol) in toluene (5 mL) was added in one portion, and the solution was shaken until all of the borane had dissolved and a white precipitate formed. The solution was warmed to room temperature, and the solvent removed under reduced pressure. The solid was washed with pentane (15 mL), dissolved in bromobenzene (10 mL), and filtered through Celite. Layering the solution with pentane (10 mL) resulted in the formation of white crystals (100 mg) of the product with one equivalent of cocrystallized bromobenzene. Cooling of the mother liquor yielded an additional crop of crystals (52%) for an overall yield of 54%. ^{1}H NMR (CD_2Cl_2): 8.1 (m, 1H, N=C(*H*)N), 7.5 (m, 1H), 7.4 (d, 2H, $^3J_{H-H}$ = 2 Hz, C(*H*)=C(*H*)), 7.3 (m, 2H), 7.2 (m, 2H), 1.6 (s, 18H, C*Me*$_3$). ^{11}B NMR (CD_2Cl_2): −20.9. ^{13}C{^{1}H} NMR (CD_2Cl_2), partial: 148.9 (dm, $^1J_{C-F}$ = 241 Hz, *o*-C_6F_5), 138.9 (dm, $^1J_{C-F}$ = 244 Hz, *p*-C_6F_5), 137.4 (dm, $^1J_{C-F}$ = 248 Hz, *m*-C_6F_5), 132.0, 129.5 (s, br, NC(*H*)N), 128.4 (s), 128.0 (s), 127.5 (s), 121.2 (s, C(*H*)=C(*H*)), 61.5 (s, *C*Me$_3$), 30.0 (s, C*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −132.6 (d, 6F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −163.7 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −167.3(t, 6F, $^3J_{F-F}$ = 22 Hz *m*-C_6F_5). Anal. Calcd for $C_{43}H_{29}BN_2F_{15}Br$ (949.410): C, 54.40; H, 3.08; N, 2.95. Found: C, 54.87; H, 3.37; N, 2.86. X-ray quality crystals were grown from slow cooling of a solution in THF.

Synthesis of *E*-Me$_2$S(Ph)C=C(H)B(C_6F_5)$_3$ (32). To a solution of $Me_2S\cdot B(C_6F_5)_3$ (50 mg, 0.09 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise PhCCH (40 mg, 0.4 mmol). The reaction mixture reddened slightly, was layered with pentane (5 mL), and was placed in a −35 °C freezer. After 24 h colorless crystals had formed, the solvent was decanted, and the crystals were dried *in vacuo* to afford a crystalline product (52 mg, 88%). ^{1}H NMR (CD_2Cl_2): 8.4 (s, 1H, C=C-*H*), 7.4 (t, 1H, $^3J_{H-H}$ = 7 Hz, *p*-Ph), 7.3 (t, 2H, $^3J_{H-H}$ = 7 Hz, *m*-Ph), 6.9 (d, 2H, $^3J_{H-H}$ = 7 Hz, *o*-Ph), 2.6 (s, 6H, SC*H*$_3$). ^{11}B NMR (CD_2Cl_2): −16.2 (s). ^{19}F NMR (CD_2Cl_2): −131.9 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −161.6 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.2 (t, 6F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5). Anal. Calcd for $C_{28}H_{12}BF_{15}S$ (676.256): C, 49.73; H, 1.79. Found: C, 49.08; H, 1.89.

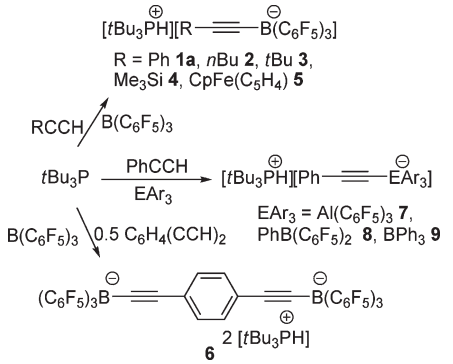
Synthesis of *E*-(PhCH$_2$)$_2$S(Ph)C=C(H)B(C_6F_5)$_3$ (33). To a solution of B(C_6F_5)$_3$ (150 mg, 0.29 mmol) and dibenzylsulfide (130 mg, 0.54 mmol) in toluene (1.5 mL) was added dropwise PhCCH (30 mg, 0.3 mmol). The reaction mixture reddened slightly, was layered with hexanes (5 mL), and was placed in a −35 °C freezer. After 24 h colorless crystals formed (237 mg, 95%). NMR studies revealed solutions of the product in CD_2Cl_2 were spectroscopically pure initially, but would decompose over ∼30 min to afford starting materials and other unidentified products. ^{1}H NMR (CD_2Cl_2): 8.4 (s, 1H, C=C-*H*), 7.5 (m, 6H, *Ph*), 7.3−7.2 (m, 7H, $^3J_{H-H}$, *m*-Ph), 6.7 (d, 2H, $^3J_{H-H}$ = 7 Hz, *o*-Ph), 4.2 (d, 2H, $^2J_{H-H}$ = 13 Hz SC*H*$_2$Ph), 3.9 (d, 2H, $^2J_{H-H}$ = 13 Hz SC*H*$_2$Ph). ^{11}B NMR (CD_2Cl_2): −16.2 (s). ^{13}C{^{1}H} NMR (255 K, CD_2Cl_2), partial: 52 mg (88%) 179.1 (m, C=*C*-B), 147.7 (dm, $^1J_{C-F}$ = 234 Hz, *o*-C_6F_5), 138.3 (dm, $^1J_{C-F}$ = 247 Hz, *p*-C_6F_5), 136.4 (dm, $^1J_{C-F}$ = 247 Hz, *m*-C_6F_5), 130.2, 129.9, 129.8, 129.6, 129.1, 128.6, 128.3, 126.9, 46.53 (s, *C*H$_2$Ph). ^{19}F NMR (CD_2Cl_2): −131.9 (d, 6F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −161.8 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.3 (t, 6F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5). Anal. Calcd for $C_{42}H_{20}BF_{15}S$ (852.495): C, 59.18; H, 2.36. Found: C, 59.39; H, 2.40.

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 Kα radiation (λ = 0.71073 Å). Data collection strategies were determined 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 using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS). Non-hydrogen atomic scattering factors were taken from the literature tabulations.[50] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen 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 $w(F_o - F_c)^2$ where the weight w 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 non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded 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 bonded. 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.

Results and Discussion

Phosphine/Borane FLPs: Deprotonation of Alkynes. We have previously communicated that the reaction of PhCCH with a mixture of *t*Bu$_3$P and B(C_6F_5)$_3$ in toluene at −35 °C results in the immediate formation of [*t*Bu$_3$PH][PhCCB(C_6F_5)$_3$] (**1a**) (Scheme 2).[51] The corresponding reactions of *t*Bu$_3$P and

Scheme 2. Synthesis of 1−9



B(C_6F_5)$_3$ with 1-hexyne, 3,3-dimethyl-1-butyne, ethynyltrimethylsilane, and ethynylferrocene afforded the complexes [*t*Bu$_3$PH][RCCB(C_6F_5)$_3$] (R = C_4H_9 **2**, *t*Bu **3**, Me_3Si **4**, and CpFe(C_5H_4) **5**), respectively (Scheme 2). Although monitoring of these reactions by NMR spectroscopy indicated that these small-scale reactions in CD_2Cl_2 were quantitative with no formation of addition products, the products **2**−**5** could only be isolated in moderate to low yields. These complexes

(50) Cromer, D. T.; Waber, J. T. *Int. Tables X-Ray Crystallogr.* **1974**, *4*, 71–147.
(51) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397.

exhibited NMR spectral parameters similar to **1a**, and the structures of **2** and **5** were confirmed by X-ray crystallography (Figure 1, Table 1). In a similar fashion, FLP deprotonation of 1,4-diethynylbenzene was employed to prepare the salt $[t\mathrm{Bu_3PH}]_2[(\mathrm{C_6F_5})_3\mathrm{BCC}(\mathrm{C_6H_4})\mathrm{CCB}(\mathrm{C_6F_5})_3]$ (**6**) (Scheme 2). This species is related to the known salt $[\mathrm{Li(THF)_4}]_2$-$[\mathrm{Ph_3BCC}(\mathrm{C_6H_4})\mathrm{CCBPh_3}]$, which draws attention as an "ionic rotor".[52]

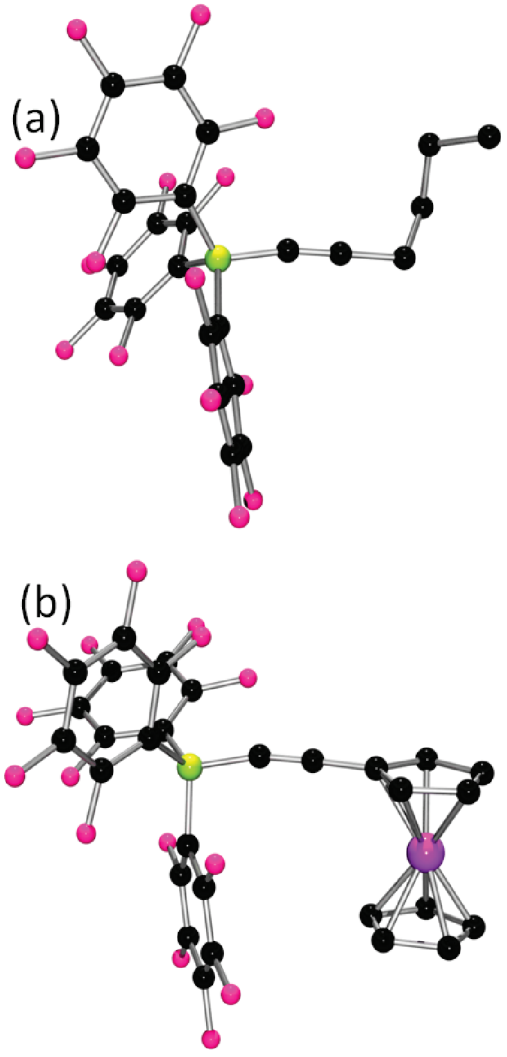


Figure 1. POV-Ray depictions of the anions of (a) **2** and (b) **5**. C: black, Fe: purple, P: orange, F: pink, B: yellow-green. H atoms are omitted for clarity.

Variation in the Lewis acid was probed. We have previously reported the formation of the aluminum analogue of **1a**, $[t\mathrm{Bu_3PH}][\mathrm{PhCCAl}(\mathrm{C_6F_5})_3]$ (**7**, Figure 2, Scheme 2),[51] which was readily formed using $\mathrm{Al}(\mathrm{C_6F_5})_3$. In a similar fashion, the mixed-aryl borane $\mathrm{PhB}(\mathrm{C_6F_5})_2$, despite having a lower Lewis acidity than $\mathrm{B}(\mathrm{C_6F_5})_3$ (as assessed by Child's method:[53] 0.54 vs 0.68),[54] also reacted with PhCCH to afford the salt $[t\mathrm{Bu_3PH}][\mathrm{PhCCBPh}(\mathrm{C_6F_5})_2]$ (**8**). Even the less Lewis acidic borane, $\mathrm{BPh_3}$, effected the same deprotonation reaction to afford $[t\mathrm{Bu_3PH}][\mathrm{PhCCBPh_3}]$ (**9**, Figure 2). In contrast, $t\mathrm{Bu_3P}\cdot\mathrm{BF_3}$ or 1:1 mixtures of $t\mathrm{Bu_3P}$ and $\mathrm{BCl_3}$ or $t\mathrm{Bu_3P}$ and $\mathrm{B}(\mathrm{OC_6F_5})_3$ showed no evidence of reaction with PhCCH. These latter observations suggest that there are

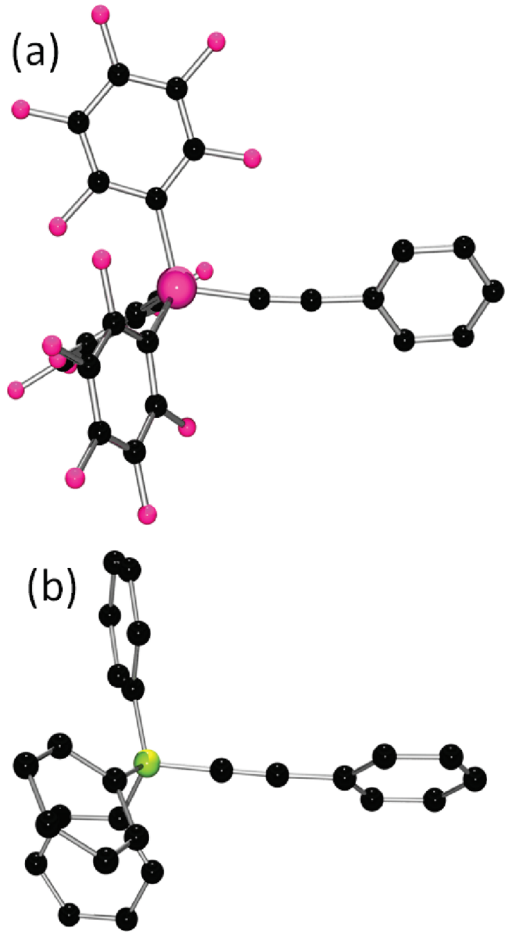


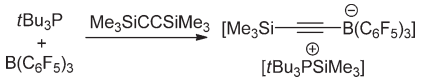
Figure 2. POV-Ray depictions of the anions of (a) **7** and (b) **9**. C: black, P: orange, Al: orchid, F: pink, B: yellow-green. H atoms are omitted for clarity.

Table 1. Selected NMR Data[a] and Metrical Parameters for Deprotonation Products 1−10

	^{11}B(^{29}Al) NMR (ppm)	^{19}F NMR $\Delta_{m\text{-}p}$ (ppm)	B(Al)−C_{sp} (Å)	C_{sp}−C_{sp} (Å)	B(Al)−C_{sp}−C_{sp} (deg)
1[c]	−20.8	3.5	1.592(3)	1.202(3)	174.7(2)
2	−20.5[b]	3.0[b]	1.592(5)	1.194(4)	170.3(3)
3	−21.0	3.2			
4	−20.8	3.4			
5	−20.8	3.4	1.589(2)	1.200(2)	166.51(16)
6	−20.9	3.2			
7[c]	103.2	5.9	1.9478(19)	1.207(2)	172.51(18)
8	17.13	2.4			
9	−12.1		1.613(2)	1.207(2)	179.16(18)
10	−21.4	3.5			

[a] Spectra recorded in $\mathrm{CD_2Cl_2}$ and reported in ppm. [b] Spectra recorded in $\mathrm{C_6D_5Br}$. [c] Data from ref 51.

Scheme 3. Synthesis of 10



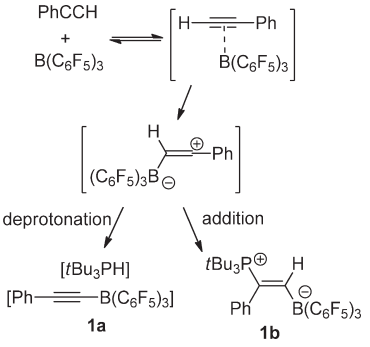
10

both a steric and electronic limits for the FLP deprotonation of terminal alkynes. Similar observations have been observed for the activation of H_2 by various FLP mixtures.

The FLP tBu$_3$P and B(C$_6$F$_5$)$_3$ was much less reactive with internal alkynes. Reactions with 2-hexyne, 3-hexyne, and 2-butyne afforded only inseparable mixtures of products, whereas combinations with PhCCPh or diphenylbutadiyne showed no evidence of reaction. These systems stand in contrast to the reaction of diisopropylbutadiyne with the linked FLP Mes$_2$PCH$_2$CH$_2$B(C$_6$F$_5$)$_2$ reported by Erker et al., which yielded an interesting, cyclic phosphonium-borate cumulene.[36] tBu$_3$P and B(C$_6$F$_5$)$_3$ did however react with an excess of Me$_3$SiCCSiMe$_3$ within minutes to give a single product, **10**. The ^{1}H NMR spectrum revealed two inequivalent Me$_3$Si groups, one of which showed H−P coupling. The formulation of **10** as the alkynylborate species [tBu$_3$PSiMe$_3$][Me$_3$SiCCB(C$_6$F$_5$)$_3$] (Scheme 3) is further evidenced by a resonance at −21.4 ppm in the ^{11}B NMR spectrum and was confirmed with preliminary crystallographic data.[55] This silylphosphonium alkynylborate was highly hygroscopic, and attempts to recrystallize the compound, even in a glovebox atmosphere, led to the isolation of **4**, consistent with the sensitivity of the silylphosphonium cation. However, solutions of **10** in CD_2Cl_2 sealed in a Teflon-capped NMR tube were stable for over a week. Treatment of **10** with additional equivalents of tBu$_3$P and B(C$_6$F$_5$)$_3$ did not effect cleavage of the Si−C bond of the silylacetylide fragment of the anion. It is noteworthy that similar phosphonium cations have been generated via the treatment of phosphines with Me$_3$SiCo(CO)$_4$.[56,57] It is also of note that base capture of a silylium cation is a critical step in the proposed mechanism of catalytic hydrosilylation of imines with B(C$_6$F$_5$)$_3$.[58]

Phosphine/Borane Addition Reactions with Alkynes. The mechanism of the deprotonation reactions described above has not been probed via kinetic study; however it is reasonable to suggest that alkyne electrophilic attack of the Lewis acid affords a transient carbocation, which in the presence of a bulky, basic phosphine such as tBu$_3$P affords the phosphonium alkynyl borates (Scheme 4). A competitive reaction would be addition of the phosphine to the carbocation, affording a zwitterionic addition product with a *trans* disposition of the P and B centers (Scheme 4). This latter mechanism is consistent with the common role of vinyl

Scheme 4. Generation of 1a and 1b



cations as intermediates in the reactions of alkynes with electrophiles.[59,60] A re-examination of the reaction affording **1a** at room temperature revealed the formation of a second minor product (**1b**) in varying and irreproducible amounts (5−20%). The latter species was characterized by a doublet in the ^{1}H NMR spectrum at 8.4 ppm with a J_{H-P} = 27 Hz, an ^{11}B NMR resonance at −16 ppm, and a multiplet in the ^{31}P{^{1}H} NMR spectrum at 44.5 ppm (Table 1). These data collectively indicate the formation of the zwitterion E-tBu$_3$P-(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (**1b**, Scheme 4), presumably formed via addition of the phosphine and borane to PhCCH. The latter species could not be isolated from **1a**, but the spectroscopic similarity to other addition complexes (*vide infra*) leaves little doubt of its formulation. In addition, variable-temperature NMR studies of solutions of initially pure **1a** in C$_6$D$_5$Br revealed partial conversion to **1b** at high temperatures (70−130 °C). Cooling such a mixture to room temperature afforded a ca. 19:1 mixture of **1a** and **1b**. Prolonged heating of these solutions (ca. 1 week at 80 °C) resulted in no further enrichment in **1b**. Increasing the temperature to 120 °C (2 h) resulted in partial loss of PhCCH and the liberation of tBu$_3$P and B(C$_6$F$_5$)$_3$. These data suggest that addition and deprotonation are reversible and competitive pathways. Thus we reasoned that FLP-alkyne addition products should be favored by bulky, less basic phosphines. Indeed, we have previously communicated that bulky, but less basic phosphines[61] such as (o-tol)$_3$P in combination with B(C$_6$F$_5$)$_3$ readily react with PhCCH to afford the addition complex E-(o-tol)$_3$P-(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (**11**) (Scheme 5). In **11**, the P and B centers are *trans* disposed about the double bond, and the P is bonded to the substituted carbon of the former alkyne.

In a similar vein, reaction of the Lewis acid-base adduct Ph$_3$P·B(C$_6$F$_5$)$_3$ with PhCCH gave the addition complex by the synthesis of E-Ph$_3$P(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (**12**), while reaction of Ph$_3$P·B(C$_6$F$_5$)$_3$ and ethynylferrocene gave E-Ph$_3$P(CpFe(C$_5$H$_4$))C=C(H)B(C$_6$F$_5$)$_3$ (**13**, Scheme 5). The latter species was crystallographically characterized (Figure 3, Table 2). Reaction of Ph$_3$P·B(C$_6$F$_5$)$_3$ with the internal alkyne 1-phenyl-2-propyne, however, did afford the addition complex E-Ph$_3$P(Ph)C=C(Me)B(C$_6$F$_5$)$_3$ (**14**), although higher temperatures were needed to facilitate this reaction. Similarly to **11**, **14** exhibited broadened NMR resonances due to restricted rotation. Above 100 °C NMR spectroscopy did not afford the limiting spectra but rather showed loss of alkyne.

The above syntheses demonstrated that this addition reactivity is not limited to bulky phosphines that form FLPs

(52) Gardinier, J. R.; Pellechia, P. J.; Smith, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 12448–12449.
(53) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801–8.
(54) Morrison, D. J.; Piers, W. E. *Org. Lett.* **2003**, *5*, 2857–2860.
(55) Repeated attempts led only to small single crystals of **9**, where the data were not of sufficient quality to merit publication.
(56) Bald, J. F., Jr.; MacDiarmid, A. G. *J. Organomet. Chem.* **1970**, *22*, C22–C24.
(57) Schaefer, H.; MacDiarmid, A. G. *Inorg. Chem.* **1976**, *15*, 848–856.
(58) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921–3923.
(59) Patai, S. *The Chemistry of the Carbon-Carbon Triple Bond*; J. Wiley: New York, 1978.
(60) Stang, P. J. *Vinyl Cations*; Academic Press: New York, 1979.
(61) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681–686.

with $B(C_6F_5)_3$. Rather isolable phosphine-borane adducts provide convenient access to this reactivity, presumable because of the existence of equilibria affording the FLP. In this vein, despite the known ability of sterically unencumbered phosphines to form classical adducts with $B(C_6F_5)_3$, the reaction of the secondary phosphines Ph_2PH or $(C_6H_2Me_3)_2PH$ or the primary phosphine $(C_6H_2tBu_3)PH_2$ with $B(C_6F_5)_3$ and PhCCH afforded the corresponding addition products *E*-$R_2PH(Ph)C{=}C(H)B(C_6F_5)_3$ (R = Ph **15**, $C_6H_2Me_3$ **16**, and $(C_6H_2tBu_3)PH_2(Ph)C{=}C(H)B(C_6F_5)_3$ **17**, Scheme 5, Figure 4).

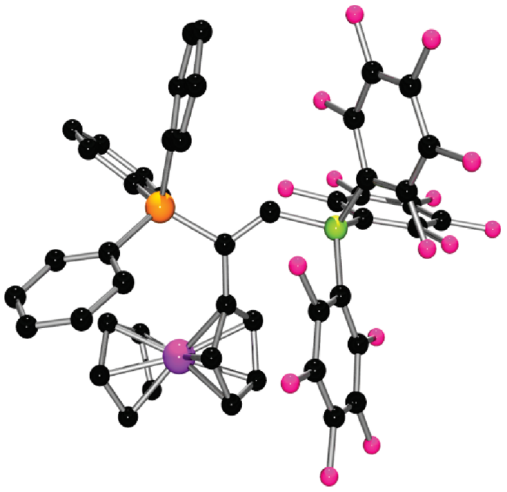
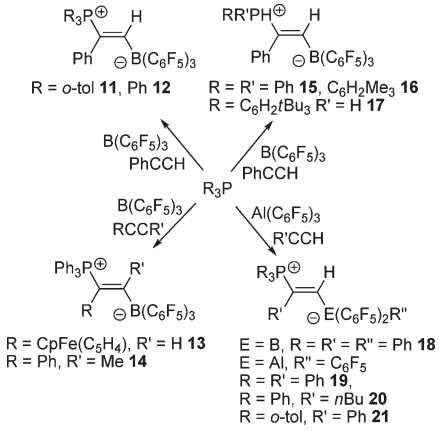


Figure 3. POV-Ray depictions of **12**. C: black, Fe: purple, P: orange, F: pink, B: yellow-green. H atoms are omitted for clarity.

Scheme 5. Synthesis of 11−21



Variation in the Lewis acid was also possible for these addition reactions. Treatment of the mixed arylborane PhB-$(C_6F_5)_2$ with Ph_3P and PhCCH afforded the complex *E*-$Ph_3P(Ph)C{=}C(H)BPh(C_6F_5)_2$ (**18**), while the analogous reaction with $PhMe{\cdot}Al(C_6F_5)_3$ afforded *E*-$Ph_3P(Ph)C{=}C(H)Al(C_6F_5)_3$ (**19**, Scheme 5). The corresponding combination of Ph_3P and $PhMe{\cdot}Al(C_6F_5)_3$ with 1-hexyne yielded *E*-$Ph_3P(C_4H_9)C{=}C(H)Al(C_6F_5)_3$ (**20**), while we also previously communicated the Al congener of **11**, *E*-$(o\text{-tol})_3P(Ph)C{=}C(H)Al(C_6F_5)_3$ (**21**) (Scheme 5).[51] Whereas the B-based zwitterionic addition products appeared to be indefinitely stable, the Al-based zwitterions proved much less stable and could be stored in the glovebox for no longer than a few weeks without decomposition.

This reactivity can be extended to provide access to macrocyclic and chain-like species. For example, the linked phosphine-borane complex $Mes_2PC_6F_4B(C_6F_5)_2$[45] was also treated with PhCCH to afford the macrocyclic species $[(H)C{=}C(Ph)Mes_2PC_6F_4B(C_6F_5)_2]_2$ (**22**, Scheme 6). The NMR spectra of this complex showed broadened resonances, and facile loss of PhCCH in solution was observed. It is unclear whether this fluxionality is due to a rapid equilibrium, restricted rotation within the molecule, or a combination of the two. However the complex could be isolated in moderate yield after treatment with an excess of PhCCH, and X-ray crystallography verified this formulation (Figure 5). Alternatively, sequential addition reactions of the $Ph_2PCH_2CH_2PPh_2$ with PhCCH and $B(C_6F_5)_3$ was probed. Indeed, the mono and bis addition products, $Ph_2PCH_2CH_2PPh_2(Ph)C{=}C(H)B(C_6F_5)_3$ (**23**) and $(CH_2PPh_2(Ph)C{=}C(H)B(C_6F_5)_3)_2$ (**24**), respectively (Scheme 6), were observed. In the case of **23**, the $^{31}P\{^1H\}$ NMR spectrum contains a doublet with a $^3J_{P-P}$ of 45 Hz attributable to the pendant phosphine and a complex multiplet attributable to the phosphonium center, which is coupled to both the pendant phosphine and the boron center. Complex **24** was not sufficiently soluble to allow for NMR characterization, but it could be isolated by crystallization and structurally characterized (Figure 6).

The related addition reaction involving 1,4-diethynylbenzene and two equivalents of $Ph_3P{\cdot}B(C_6F_5)_3$ afforded only the monoaddition zwitterion *E*-$HC{\equiv}CC_6H_4C(PPh_3){=}C(H)B(C_6F_5)_3$ (**25**, Scheme 7), even after several weeks. The corresponding reaction with one equivalent of $Ph_3P{\cdot}B(C_6F_5)_3$ afforded **25** in good yield and permitted crystallographic characterization (Figure 7). Given the geometry,

Table 2. Selected NMR Data[a] and Bond Lengths of Addition Products 11−21, 32, and 33

	^{11}B (^{29}Al) NMR (ppm)	^{19}F NMR $\Delta_{m\text{-}p}$ (ppm)	^{31}P NMR (ppm)	B(Al)−C(=C) (Å)	P(S)−C(=C) (Å)	C=C (Å)
11[c]	−13.6[b]	4.0[b]	31.1[b]	1.642(3)	1.829(2)	1.346(3)
12[c]	−16.3	4.3	25.2	1.6393(18)	1.8056(13)	1.3451(18)
13	−16.3	4.3	23.4	1.638(2)	1.8001(14)	1.348(2)
14	−13.0		16.5			
15	−16.1	4.4	144	1.635(6)	1.787(4)	1.350(5)
16	−15.6	4.3	12.9	1.641(2)	1.8139(15)	1.347(2)
17	−16.3	4.4	−31.1	1.640(2)	1.7991(13)	1.3445(18)
18	−12.6	3.2	24.9	1.6350(14)	1.8008(10)	1.3483(13)
19	115.0	6.3	23.4	2.003(2)	1.815(2)	1.349(3)
20	114.7	6.5	23.0	1.9984(16)	1.8033(15)	1.336(2)
21[c]	116.5[b]	6.3[b]	26.13[b]	2.0040(19)	1.8199(17)	1.341(3)
32	−16.2	4.6		1.640(2)	1.8027(16)	1.333(2)
33[c]	−16.2	4.5		1.631(4)	1.798(3)	1.337(4)

[a] Spectra recorded in CD_2Cl_2 at 25 °C. [b] Spectra recorded in $C_2D_2Cl_4$ at 385 K. [c] Data from ref 51.

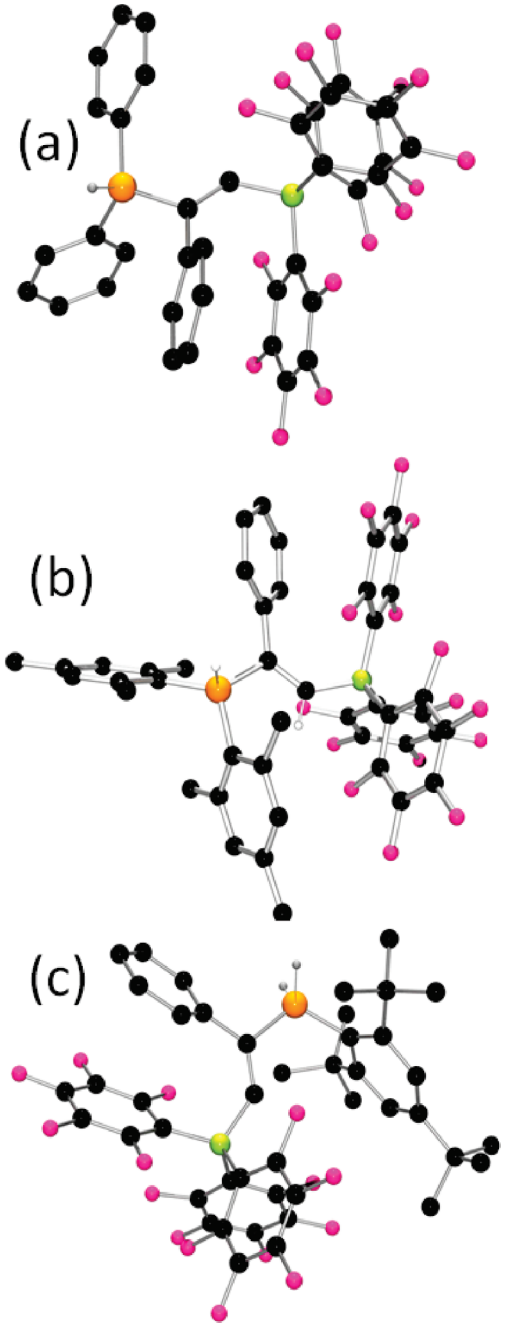


Figure 4. POV-Ray depictions of (a) **15**, (b) **16**, and (c) **17**. C: black, P: orange, F: pink, B: yellow-green. Most H atoms are omitted for clarity.

the difficulty with a second addition reaction may be a result of steric crowding as well as the electron perturbation resulting from the presence of the zwitterionic unit on the arene ring. It is interesting, however, that subsequent treatment of **25** with an additional equivalent of tBu$_3$P and B(C_6F_5)$_3$ yielded the unusual salt/zwitterion [tBu$_3$PH]-[(C_6F_5)$_3$BCC$_6$H$_4$C(PPh$_3$)=C(H) B(C_6F_5)$_3$] (**26**, Scheme 7).

Nitrogen Base/Borane FLP Reactions with Alkynes. The corresponding reactions of nitrogen bases, B(C_6F_5)$_3$, and terminal alkynes are not without precedent. Berke and co-workers reported the deprotonation reactions of alkynes with B(C_6F_5)$_3$ and 2,6-lutidene or 2,2,5,5-tetramethylpiperidine,[41] while we have reported the intramolecular addition cyclization of *ortho*-ethynylaniline with B(C_6F_5)$_3$ to give a cyclic

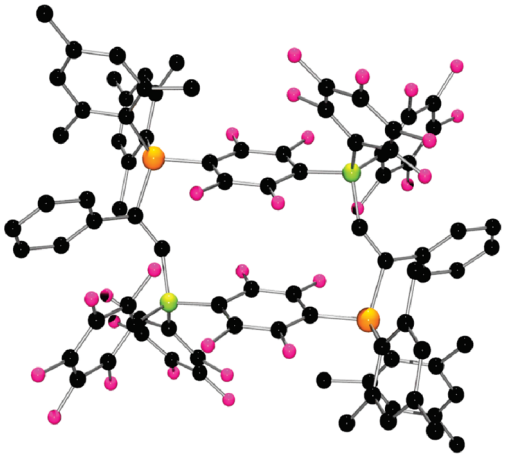


Figure 5. POV-Ray depiction of **22**. C: black, P: orange, F: pink, B: yellow-green. H atoms and cocrystallized solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): P−C(=C), 1.859(2); B−C(=C), 1.657(3); C=C, 1.345(3).

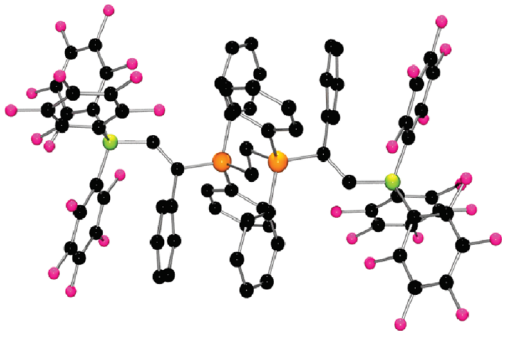
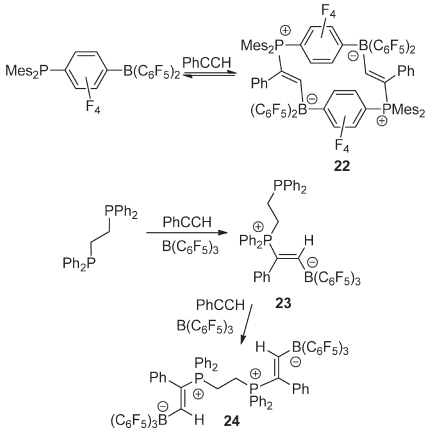


Figure 6. POV-Ray depiction of **24**. C: black, P: orange, F: pink, B: yellow-green. H atoms and cocrystallized solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): P−C(=C), 1.790(3); B−C(=C), 1.629(4); C=C, 1.342(4).

Scheme 6. Synthesis of 22−24



anilinium-borate.[62] Interestingly, herein we report the corresponding reaction of benzyldimethylamine with PhCCH

(62) Voss, T.; Chen, C.; Kehr, G.; Nauha, E.; Erker, G.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16* (3005−3008), S3005/1–S3005/7.

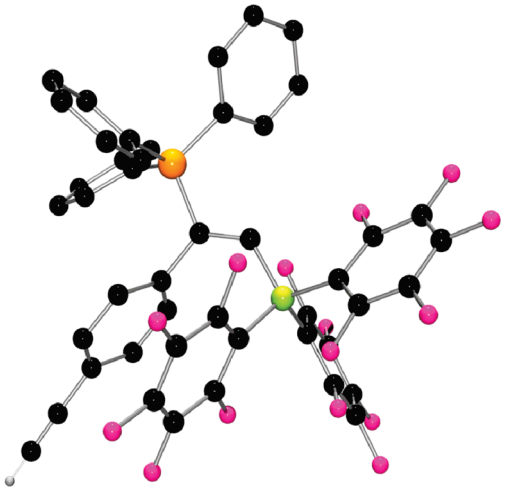
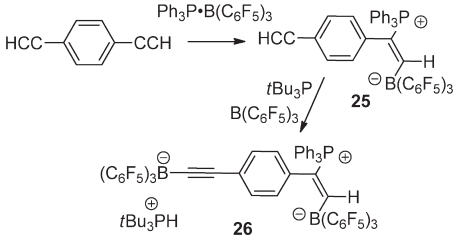
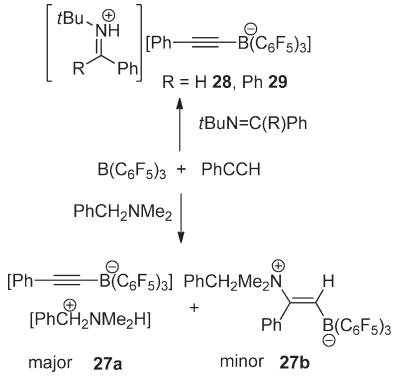


Figure 7. POV-Ray depiction of **25**. C: black, P: orange, F: pink, B: yellow-green. Most H atoms and cocrystallized solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): P−C(=C), 1.802(3); B−C(=C), 1.641(5); C=C, 1.344(5); C≡C, 1.180(7).

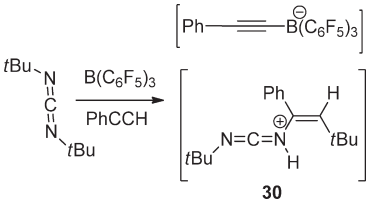
Scheme 7. Synthesis of 25 and 26



Scheme 8. Synthesis of 27−29



Scheme 9. Synthesis of 30



and $B(C_6F_5)_3$, which is shown by NMR spectroscopy to give a 84:16 mixture of both deprotonation and addition products, $[PhCH_2NMe_2H][PhCCB(C_6F_5)_3]$ (**27a**) and $PhCH_2NMe_2(Ph)C{=}C(H)B(C_6F_5)_3$ (**27b**), respectively (Scheme 8).

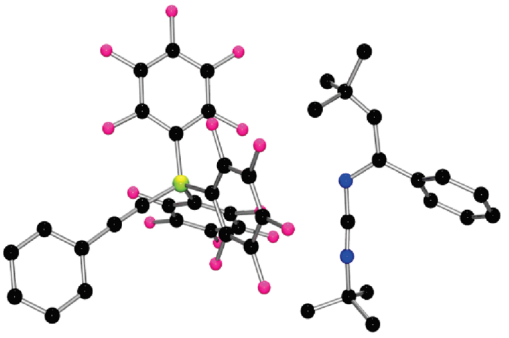


Figure 8. POV-Ray depiction of **30**. C: black, F: pink, N: aquamarine, B: yellow-green, H: white. Most H atoms and cocrystallized solvent are omitted for clarity.

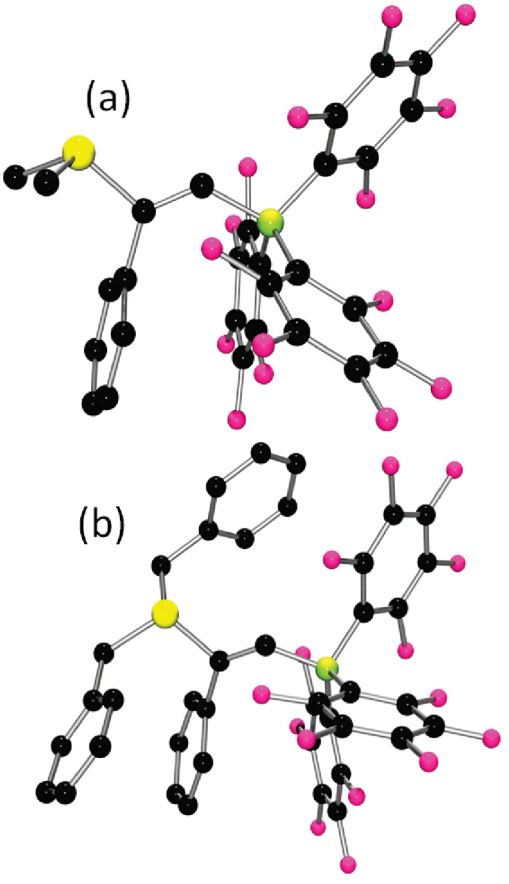


Figure 9. POV-Ray depiction of (a) **32** and (b) **33**. C: black, S: yellow: F: pink, B: yellow-green. H atoms and cocrystallized solvent are omitted for clarity.

Scheme 10. Synthesis of 31−33

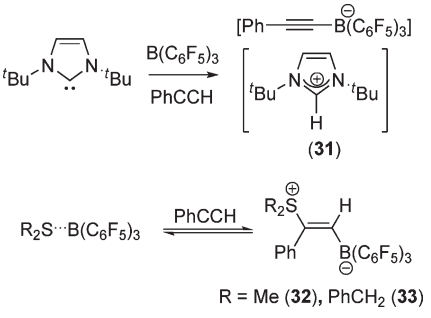


Table 3. Crystallographic Parameters[a]

	2	**5**	**7**	**9**	**13**	**15**	**16**
formula	$C_{36}H_{37}BF_{15}P$	$C_{42}H_{37}BF_{15}FeP$	$C_{38}H_{32}BF_{15}P\cdot 1/2C_6H_5Cl$	$C_{38}H_{48}BP$	$C_{48}H_{25}BF_{15}FeP\cdot 1/2CH_2Cl_2$	$C_{38}H_{17}BF_{15}P\cdot 1/2CH_2Cl_2$	$C_{44}H_{29}BF_{15}P\cdot CH_2Cl_2$
fw	796.44	924.35	887.61	546.54	1026.76	842.76	969.38
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	*Pcba*	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	20.0199(10)	12.1738(9)	12.5867(4)	12.3110(11)	10.9787(4)	10.7515(9)	12.3010(4)
b (Å)	16.7127(7)	12.6282(9)	16.6533(5)	13.8672(13)	21.7431(7)	19.2509(18)	12.8632(4)
c (Å)	21.5983(8)	13.9670(11)	19.4595(6)	19.2209(16)	17.9889(6)	19.5755(18)	15.2230(5)
α (deg)	90	77.682(2)	90	90	90	60.875(5)	74.3200(10)
β (deg)	90	79.434(2)	100.5490(10)	103.184(5)	91.597(2)	84.592(5)	67.2090(10)
γ (deg)	90	73.091(2)	90	90	90	84.082(5)	69.473(2)
V (Å^3)	7226.5(5)	1990.1(3)	4010.0(2)	3194.9(5)	4292.5(3)	3516.0(5)	2054.31(11)
Z	8	2	4	4	4	4	2
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
d(calc) gcm^{-3}	1.462	1.543	1.470	1.136	1.587	1.592	1.567
μ, mm^{-1}	0.180	0.521	0.224	0.111	0.553	0.264	0.300
data collected	35330	66034	35412	52184	71683	79398	42915
R_{int}	0.1112	0.0333	0.0324	0.0686	0.0445	0.0755	0.0295
data used	8286	9039	9205	7315	15 485	11 269	11 716
variables	491	674	554	374	628	1026	581
R ($>2\sigma$)	0.0584	0.0344	0.0406	0.0456	0.0620	0.0574	0.0438
wR_2	0.1371	0.0951	0.1079	0.1077	0.2109	0.1746	0.1290
GOF	0.972	1.056	1.034	1.002	1.047	1.024	1.039

	17	**18**	**19**	**20**	**22**	**24**	**25**	**27a**	**29**
formula	$C_{44}H_{37}BF_{15}P$	$C_{44}H_{26}BF_{10}P\cdot 1/2CH_2Cl_2$	$C_{44}H_{21}AlF_{15}P\cdot 1/2C_6H_5Br$	$C_{37}H_{21}AlF_{15}P$	$C_{88}H_{56}BF_{28}P_2\cdot PhMe$	$C_{78}H_{36}B_2F_{30}P_2\cdot 2CH_2Cl_2$	$C_{46}H_{21}BF_{15}P\cdot 2.5CH_2Cl_2$	$C_{35}H_{19}BF_{15}N$	$C_{43}H_{25}BF_{15}N$
fw	892.52	828.89	971.07	872.57	1821.04	898.24	1112.72	749.32	851.45
cryst syst	monoclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$
a (Å)	11.6919(8)	10.6158(5)	11.6961(8)	9.9634(11)	20.9887(11)	12.5795(7)	12.1892(8)	11.4843(7)	45.9136(16)
b (Å)	17.9236(11)	10.9157(5)	12.6086(10)	11.2388(13)	20.5295(11)	18.1504(9)	18.2218(11)	13.1053(10)	10.2766(4)
c (Å)	19.8532(11)	18.9691(10)	14.700(1)	19.821(2)	18.5092(10)	16.3457(9)	22.5003(14)	21.4793(15)	32.6110(11)
α (deg)	90	87.183(3)	106.702(3)	74.086(6)	90	90	90	90	90
β (deg)	94.709(3)	74.873(2)	100.881(3)	87.361(5)	96.190(4)	99.017(4)	103.203(3)	103.838(4)	103.102(2)
γ (deg)	90	65.677(2)	90.595(4)	65.541(5)	90	90	90	90	90
V (Å^3)	4146.4(5)	1929.35(16)	2034.2(3)	1937.1(4)	7928.9(7)	3686.0(3)	4865.4(5)	3138.9(4)	14986.5(0)
Z	4	2	2	2	4	2	4	4	16
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
d(calc) (g cm^{-3})	1.430	1.416	1.580	1.496	1.517	1.619	1.569	1.586	1.509
μ (mm^{-1})	0.166	0.154	0.685	0.197	0.172	0.327	0.424	0.155	0.140
data collected	121 123	90 045	73 453	35 965	66 604	43 972	63 390	50 804	137 008
R_{int}	0.0414	0.0338	0.0520	0.0378	0.0420	0.0741	0.0399	0.0630	0.0457
data used	10 116	19 019	15 379	8848	9158	8349	12 629	8931	18 397
variables	567	532	586	533	555	532	649	471	1095
R ($>2\sigma$)	0.0357	0.0461	0.0654	0.0366	0.0597	0.0547	0.0890	0.0527	0.0518
wR_2	0.0965	0.1375	0.2173	0.1103	0.1742	0.1551	0.2974	0.1593	0.1426
GOF	1.013	1.017	1.036	1.058	1.043	1.023	1.057	1.028	1.016

	30	**31**	**32**	**33**
formula	$C_{43}H_{30}BN_2F_{15}\cdot 1/2C_6H_5Cl$	$C_{37}H_{26}BF_{15}N_2$	$C_{28}H_{12}BF_{15}S$	$C_{40}H_{20}BF_{15}S1/2C_6H_{14}$
fw	926.27	794.41	676.25	871.52
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	11.2560(7)	12.4344(4)	20.2284(14)	9.9881(3)
b (Å)	12.2232(8)	13.5100(4)	14.5997(10)	11.0871(4)
c (Å)	16.5685(11)	24.1219(7)	18.3315(12)	17.1835(6)
α (deg)	104.065(4)	90	90	82.846(2)
β (deg)	107.259(4)	98.576(2)	104.952(3)	74.407(2)
γ (deg)	90.364(4)	90	90	85.779(2)
V (Å^3)	2104.1(2)	4006.9(2)	5230.5(6)	1816.98(11)
Z	2	4	8	2
T (K)	150(2)	150(2)	150(2)	150(2)
d(calc) (g cm^{-3})	1.462	1.343	1.718	1.558
abs coeff, *μ* (mm^{-1})	0.162	0.128	0.251	0.199
data collected	34 343	35 245	148 855	26 701
R_{int}	0.0459	0.0579	0.0627	0.0518
data used	9768	9095	12 866	7604
variables	592	502	815	526
R ($>2\sigma$)	0.0901	0.0659	0.0352	0.0532
wR_2	0.2830	0.2033	0.0851	0.1445
GOF	1.081	1.154	1.012	1.015

[a] Data collected Mo Kα radiation (*λ* = 0.71073 Å).

Although these species give rise to the characteristic ^{11}B NMR resonances at −20.8 and −16.4 ppm, respectively, only the former could be isolated and fully characterized. The structure of **27a** was confirmed crystallographically. In a similar fashion, the imines *t*BuN=CHPh and *t*BuN=CPh$_2$ react quantitatively with PhCCH and B(C$_6$F$_5$)$_3$ to afford the iminium-alkynylborate salts [(*t*Bu)HN=CHPh][PhCCB(C$_6$F$_5$)$_3$] (**28**) and [(*t*Bu)HN=CPh$_2$][PhCCB(C$_6$F$_5$)$_3$] (**29**), respectively (Scheme 8). Spectral parameters were as expected, and the structure of **29** was unambiguously confirmed by crystallographic methods. Transformation of **28** and **29** to the borane adducts of the corresponding propargylamines via thermolytic phenylacetylide transfer from boron to the activated iminium cation was explored. Although ^{11}B NMR and ^{19}F NMR spectra were consistent with acetylide transfer to the iminium cation, efforts to isolate these species were unsuccessful.

In a final example of a nitrogen base reaction, *t*BuNCN*t*-Bu, B(C$_6$F$_5$)$_3$, and two equivalents of PhCCH were combined. This resulted in several products; however the major product (**30**, Scheme 9) was isolated as a crystalline solid in 64% yield. The nature of this species was confirmed crystallographically (Figure 8), and it was consistent with concurrent addition and deprotonation reactions. The product **30**, formulated as [*t*BuNCN(H)C(Ph)=C(H)*t*Bu][PhCCB(C$_6$F$_5$)$_3$], appears to result from both deprotonation and addition reactions with PhCCH, although the order of reaction remains unclear. One possible sequence involves deprotonation of PhCCH and addition of the resulting iminium to a second equivalent of alkyne with proton and *t*Bu group migration (Scheme 9). This unusual reaction was reproducible, although this reactivity could not be extended to other carbodiimides.

Non-pnictogen Lewis Bases and FLP Reactions with Alkynes. It has been previously demonstrated that N-heterocyclic carbenes (NHCs) can be used as the Lewis base in an FLP to effect both H−H and N−H bond cleavage.[22,63] Thus, B(C$_6$F$_5$)$_3$ was added to a mixture of 1,3-di-*tert*-butylimidazolin-2-ylidene and PhCCH at −78 °C, resulting in the facile formation of the corresponding deprotonation product [(*t*BuN)$_2$C$_3$H$_3$][PhCCB(C$_6$F$_5$)$_3$] (**31**, Scheme 10), as evidenced by spectroscopic data. This thermally stable product was also characterized by X-ray crystallography. The formation of this deprotonation product is consistent with the strong Bronsted basicity of the carbene.

Sulfides are generally considered to be both poor Bronsted and Lewis bases and, in that sense, at the opposite end of the spectrum of donor ligands from carbenes. Nonetheless, they do form adducts with the strongly electrophilic B(C$_6$F$_5$)$_3$. Addition of PhCCH to a solution of Me$_2$S·B(C$_6$F$_5$)$_3$ afforded the zwitterion *E*-Me$_2$S(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (**32**, Scheme 10). Although solutions of **32** in CD$_2$Cl$_2$ were initially spectroscopically clean, after 30 min at room temperature formation of some Me$_2$S·B(C$_6$F$_5$)$_3$ and the products of the reaction of B(C$_6$F$_5$)$_3$ and PhCCH were observed in solution, illustrating that this reaction was reversible at room temperature. Nonetheless, the solid-state molecular structure of **32** was determined (Figure 9), revealing a S−C$_{sp^2}$ bond length of 1.8027(16) Å and C=C and B−C$_{sp^2}$ bond lengths similar to those of the phosphine addition complexes (*vide supra*). The corresponding reaction with (PhCH$_2$)$_2$S was also probed. This sulfide and B(C$_6$F$_5$)$_3$ form a weak adduct in CD$_2$Cl$_2$, as evidenced by a broad resonance in the ^{11}B NMR spectrum at 0.5 ppm, and consequently this adduct was not isolated. Thus combination of B(C$_6$F$_5$)$_3$, PhCCH, and excess (PhCH$_2$)$_2$S afforded the sulfonium-borate zwitterion *E*-(PhCH$_2$)$_2$S(Ph)C=C(H)B(C$_6$F$_5$)$_3$ (33, Scheme 10) in moderate yield. This species was stable for at least one hour in CD$_2$Cl$_2$ at −30 °C, but at room temperature the reaction was readily reversible, ultimately yielding the vinyl-boranes that are derived from reaction of PhCCH and B(C$_6$F$_5$)$_3$ alone. The species **33** was also characterized by X-ray diffraction studies (Figure 9) and exhibited metrical parameters similar to **32**. The reversibility of the formation of these sulfonium salts may be exploited. Addition of one equivalent of Ph$_3$P to **33** resulted in the initial precipitation of the adduct Ph$_3$P·B(C$_6$F$_5$)$_3$, which upon standing for 24 h gave quantitative conversion to **12**. In a related sense, addition of *t*Bu$_3$P afforded a mixture of **1a** and **1b**. It is also noteworthy that related sulfonium-borate zwitterions are thought to be intermediates in the homologation reactions of boranes via the alkylation of organoborane-thioethers with iodomethane.[64] In the latter case however, the salts contain a single C atom between S and B and were not isolable.

Conclusions. The reactions of FLPs with terminal alkynes afford either phosphonium-alkynylborate salts, resulting from deprotonation of the alkyne, or zwitterions, resulting from addition of both the Lewis acid and base. In addition, despite the formation of classical Lewis adducts by some donors, this FLP reactivity is still accessible. Indeed, the range of Lewis bases that participate in this reactivity was expanded to include secondary and primary phosphines, carbenes, and thioethers. Similarly the range of Lewis acids was broadened to include Al(C$_6$F$_5$)$_3$, PhBP(C$_6$F$_5$)$_2$, and B(C$_6$F$_5$)$_3$. In general the products were found to be quite stable, although in several cases the addition reactions were demonstrated to be reversible. In addition, we have observed the first Si−C cleavage effected by an FLP and the first FLP with a S-based nucleophile.

The reactivity of the products is a subject of continuing interest. In particular, we are exploring the utility of the products of primary and secondary phosphine reactions, as these species offer unique routes to anionic phosphines. We are also pursuing the utility of this reactivity in developing reagents for further use in subsequent organic transformations.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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