Supplementary Data for:

Terminal Alkyne Activation by Frustrated and Classical Lewis Acid/Phosphine Pairs

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General considerations: All manipulations were performed on a double manifold N_2/vacuum line with Schlenk-type glassware or in an N_2-filled M-Braun or Vac Atmospheres glove box. Solvents (Aldrich) were dried using an Innovative Technologies solvent system. NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer and spectra were referenced to residual solvent (^{1}H, ^{13}C) or externally (^{11}B: BF_3OEt_2, ^{19}F: $CFCl_3$, ^{27}Al: $Al(NO_3)_3$) . NMR solvents were purchased from Cambridge Isotopes, dried over CaH_2 or Na/benzophenone, vacuum distilled prior to use and stored over 4Å molecular sieves in the glovebox. $B(C_6F_5)_3$ was generously provided by Nova Chemicals. (PhMe)·$Al(C_6F_5)_3$ and Ph_3P·$B(C_6F_5)_3$ were prepared following literature methods (see citations in paper). *t*Bu_3P and (*o*-$C_6H_4Me)_3P$ were purchased from the Strem Chemical Co and used as received.

Synthesis of [*t*Bu_3PH][PhC≡C$B(C_6F_5)_3$] (1), [*t*Bu_3PH][PhC≡C$Al(C_6F_5)_3$] (2) *E*-((*o*-$C_6H_4Me)_3$P)C(Ph)=C(H)$B(C_6F_5)_3$ (3), *E*-((*o*-$C_6H_4Me)_3$P)C(Ph)=C(H)$Al(C_6F_5)_3$ (4) 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 *t*Bu_3P (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 colourless,

crystalline solid (805 mg, 75%), layering of the supernatant PhCl with pentane (3 mL) afforded an additional 75 mg of product for an overall yield of 82%.^{1}H NMR (CD_2Cl_2): 7.32 (m, 2H, *o*-Ph), 7.21 (tt, 2H, $^{3}J_{H-H}$= 7 Hz, $^{4}J_{H-H}$ = 1 Hz, *m*-Ph), 7.15 (tt, 1H, $^{3}J_{H-H}$ = 7 Hz, $^{4}J_{H-H}$ = 1 Hz, *p*-Ph), 4.80 (d, 1H, $^{1}J_{H-P}$ = 428 Hz, $^{t}Bu_3PH$), 1.52 (d, 27H, $^{3}J_{H-P}$ = 16 Hz, $^{t}Bu_3PH$). ^{11}B NMR(CD_2Cl_2): -20.78 (s). $^{13}C\{^{1}H\}$ NMR(CD_2Cl_2), partial: 148.85 (dm, $^{1}J_{C-F}$ = 245 Hz, *o*-C_6F_5), 138.88 (dm, $^{1}J_{C-F}$ = 248 Hz, *p*-C_6F_5), 137.18 (dm, $^{1}J_{C-F}$ = 241 Hz, *m*-C_6F_5), 131.80, 128.62, 128.19 (s, *ipso*-Ph), 126.64, 37.98 (d, $^{1}J_{C-P}$ = 27 Hz, P*C*Me$_3$), 30.25 (s, PC*Me*$_3$). ^{19}F NMR (CD_2Cl_2): -132.73 (d, 6F, $^{3}J_{F-F}$ = 25 Hz, *o*-C_6F_5), -163.94 (t, 3F, $^{3}J_{F-F}$ = 20 Hz, *p*-C_6F_5), -167.45 (d, 6F, $^{3}J_{F-F}$ = 19 Hz, *m*-C_6F_5). $^{31}P\{^{1}H\}$ NMR(CD_2Cl_2): 61.49. C, H analysis calc 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): 61 mg (91%), ^{1}H 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, $^{1}J_{H-P}$ = 426 Hz, $^{t}Bu_3PH$), 1.60 (d, 27H, , $^{3}J_{H-P}$ = 16 Hz, $^{t}Bu_3PH$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2), partial: 150.45 (dm, $^{1}J_{C-F}$ = 230 Hz, *o*-C_6F_5), 140.71 (dm, $^{1}J_{C-F}$ = 246 Hz, *p*-C_6F_5), 136.86 (dm, $^{1}J_{C-F}$ = 246 Hz, *m*-C_6F_5), 131.80, 128.62, 128.19, 126.64, 38.18 (d, $^{1}J_{C-P}$ = 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, $^{3}J_{F-F}$ = 20 Hz, *p*-C_6F_5), -164.44 (m, 6F, *m*-C_6F_5). ^{27}Al NMR (CD_2Cl_2): 105.18. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): 61.76. C, H analysis calc 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 **(2)**$\cdot$(C_6H_5Cl) were grown by slow cooling of a solution in chlorobenzene.

(3) : 423 mg, 75%, ^{1}H NMR ($C_2D_2Cl_4$, 385K): 8.18 (d, 1H, $^{3}J_{H-P}$ = 40 Hz, =C-*H*), 7.85 (dd, 3H, J_{H-P} = 14 Hz, $^{3}J_{H-H}$ = 7 Hz), 7.67 (t, 3H, $^{3}J_{H-H}$J = 8 Hz), 7.49 (t, 2H, $^{3}J_{H-H}$ = 7 Hz), 7.33 (dd, 3H, J_{H-P} = 8 Hz, $^{3}J_{H-H}$ = 8 Hz), 7.08 (t, 1H, $^{3}J_{H-H}$ = 7 Hz, *p*-Ph), 6.93 (m, 4H, Ph), 1.80 (s, 9H,

PC_6H_4Me). ^{11}B NMR ($C_2D_2Cl_4$, 385K): -13.55 (d, $^3J_{B-P}$ = 16 Hz). ^{19}F NMR ($C_2D_2Cl_4$, 385K): -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 ($C_2D_2Cl_4$, 385K): 31.09 (q, $^3J_{P-B}$ = 16 Hz). ^1H NMR (CD_2Cl_2, 215K): (Ratio of minor : major = 1: 1.7) 8.49 (d, 1 H, $^3J_{H-P}$ = 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_6H_4Me of minor isomer), 2.34 (s, 3H, *o*-C_6H_4Me of major isomer), 1.73 (s, 3H, *o*-C_6H_4Me of minor isomer), 1.68 (s, 3H, *o*-C_6H_4Me of minor isomer), 1.58 (s, 3H, *o*-C_6H_4Me of major isomer), 0.55 (s, 3H, *o*-C_6H_4Me of major isomer). ^{11}B NMR (CD_2Cl_2, 215K): -15.35 (s), -15.75 (s). ^{19}F NMR (CD_2Cl_2, 215K): -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, 215K): (Ratio of minor : major 1: 1.75) 30.52 (s, br, major), 27.05 (s, br, minor). ^{31}P {^1H} NMR (THF-d_8, 215K): (Ratio of minor : major 1: 2.15) 30.80 (s, br, major), 27.41 (s, br, minor). C, H analysis calc 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 **(3)**$^{\cdot}$(C_6H_5Br) were grown by slow cooling of a solution in bromobenzene.

(4): 73 mg, 84%, ^1H NMR ($C_2D_2Cl_4$, 385K): 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 ($C_2D_2Cl_4$, 385K): -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 ($C_2D_2Cl_4$, 385K): 116.52 (s, br). ^{31}P {^1H} NMR ($C_2D_2Cl_4$, 385K): 26.13 (s, br). C, H analysis calc 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 **(4)**·(CH_2Cl_2) were grown by slow evaporation of a solution in dichloromethane.

Synthesis of *E*-(Ph_3P)C(Ph)=C(H)B(C_6F_5)$_3$ (5) Phenyl acetylene (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 2 h 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 (98 mg, 87%). ^{1}H NMR (CD_2Cl_2): 8.32 (d, 1H, $^3J_{H\text{-}P}$ = 36 Hz, C=C-*H*), 7.75 (td, 3H, $^3J_{H\text{-}H}$ = 8 Hz, $^5J_{H\text{-}p}$ = 2 Hz, *p-Ph*P), 7.56 (td, 6H, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}p}$ = 6 Hz, *m-Ph*P), 7.39 (m, 6H, *o-Ph*P). ^{11}B NMR (CD_2Cl_2): -16.27 (d, $^3J_{B\text{-}P}$ = 14 Hz). ^{13}C 148.09{^{1}H} NMR (CD_2Cl_2) partial: (dm, $^1J_{C\text{-}F}$ = 236 Hz, *o*-C_6F_5), 138.44 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *m*-C_6F_5), 136.45 (dm, $^1J_{C\text{-}F}$ = 246 Hz, *p*-C_6F_5), 134.57 (d, $^3J_{C\text{-}P}$ = 10 Hz, *m-Ph*P), 134.42 (d, $^4J_{C\text{-}P}$ = 3 Hz, *p-Ph*P), 129.62 (d, $^2J_{C\text{-}P}$ = 12 Hz, *o-Ph*P), 129.25 (d, $^3J_{C\text{-}P}$ = 5 Hz, *o-Ph*C), 127.94 (d, $^4J_{C\text{-}P}$ = 2 Hz, *m-Ph*C), 127.80 (d, $^5J_{C\text{-}P}$ = 2 Hz, *p-Ph*C), 119.47 (d, $^1J_{C\text{-}P}$ = 86 Hz, P-*C*=C). ^{19}F NMR (C_6D_5Br): -130.55 (d, 6F, J = 23 Hz, *o*-C_6F_5), -160.80 (t, 3F, J = 21 Hz, *p*-C_6F_5), -165.13 (d, 6F, J = 20 Hz, *m*-C_6F_5). ^{31}P {^{1}H} NMR (CD_2Cl_2): 25.23 (q, $^3J_{P\text{-}B}$ = 15 Hz). C, H analysis calc for $C_{47}H_{27}BF_{15}P$ (876.414): C, 60.30; H, 2.42. Found: C, 60.65; H, 2.72.