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New Strategies to Phosphino–Phosphonium Cations and Zwitterions

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Dedicated to Professor M. Lappert on the occasion of his 80th birthday

Abstract: By employing strategies based on frustrated Lewis pair chemistry, new routes to phosphino-phosphonium cations and zwitterions have been developed. $B(C_6F_5)_3$ is shown to react with H_2 and P_2tBu_4 to effect heterolytic hydrogen activation yielding the phosphino-phosphonium borate salt $[(tBu_2P)PHtBu_2]$ $[HB(C_6F_5)_3]$ (**1**). Alternatively, alkenylphosphino-phosphonium borate zwitterions are accessible by reaction of $B(C_6F_5)_3$ and PhC≡CH with P_2Ph_4, P_4Cy_4, or P_5Ph_5 affording the species $[(Ph_2P)P(Ph)_2C(Ph)=C(H)B(C_6F_5)_3]$ (**2**), $[(P_3Cy_3)P(Cy)-C(Ph)=C(H)B(C_6F_5)_3]$ (**3**), and $[(P_4Ph_4)P(Ph)C(Ph)=C(H)B(C_6F_5)_3]$ (**4**). A related phosphino-phosphonium borate species—$[(Ph_4P_4)P(Ph)C_6F_4B-(F)(C_6F_5)_2]$ (**5**) is also isolated from the thermolysis of $B(C_6F_5)_3$ and P_5Ph_5.

Keywords: alkyne activation · hydrogen activation · main group elements · phosphino-phosphonium · phosphorus · zwitterions

Introduction

There has been a surge in the interest in main-group chemistry in the last decade. Much of this has been a result of the discovery of facile routes to unusual oxidation states or coordination geometries as well as the unveiling of new reactivity and unprecedented application of main group compounds in catalysis. While this renaissance has involved many other main group elements, P in particular has attracted much attention. Among a number of very recent papers that have contributed to the excitement in phosphorus chemistry,[1] Cummins et al.[2] have developed creative and elegant metal-mediated syntheses of the various $P_{4-x}As_x$ species; Shaffer et al.[3] have reported the characterization of nanostructures derived from elemental P, and the groups of Robinson and Bertrand have unveiled new P-based chains[4] and clusters[5] stabilized by carbene ligands.[6] Despite the focus of this recent flurry of activity on systems incorporating P–P bonds, related neutral and anionic polyphosphines were pioneered by Baudler and co-workers in the 1960s and 1970s.[7] In the 1980s Schmidpeter et al.[8] and Schmutzler et al.[9] reported dicationic species of the form $[(R_3P)_2PH]^{2+}$, while several other groups described the generation of phosphino-phosphonium monocations of the form $[R_3PPR_2]^+$.[10] Over the past decade, Burford and co-workers have reported an extensive series of linear and cyclic polyphosphino-phosphonium mono and dications.[11] These syntheses have been achieved by direct alkylation or by halide abstraction from chlorophosphine in the presence of a tertiary phosphine. Very recently, Weigand et al.[12] have extended this chemistry to intercept phosphenium cations with P_4, and thereby developing a clever approach to the cationic clusters $[Ph_2P_5]^+$, $[Ph_4P_6]^{2+}$, and $[Ph_6P_7]^{3+}$.

We have recently shown that in systems where classical Lewis acid–base adduct formation can be precluded by the use of sterically demanding Lewis donors and acceptors, unprecedented reactivity can result.[13] For example, such "frustrated Lewis pairs" have been shown to afford unusual aromatic substitution products[14] as well as exhibit unique reactivity with H_2,[14b,15] olefins,[16] alkynes,[17] CO_2,[18] and N_2O.[19] Herein, we demonstrate that diphosphines P_2R_4 (R = *t*Bu, Ph) and cyclic polyphosphines P_4Cy_4 and P_5Ph_5 react with the Lewis acid $B(C_6F_5)_3$ effecting H_2 or alkyne activation, as well as with $B(C_6F_5)_3$ alone under thermolysis conditions. This presents new synthetic routes to functionalized phosphino-phosphonium salts and zwitterions.

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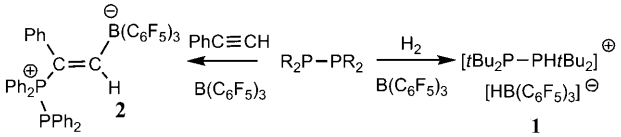
Results and Discussion

$B(C_6F_5)_3$ and P_2tBu_4 were shown to behave as a frustrated Lewis pair, as there was no apparent interaction between

these Lewis basic centers and the borane Lewis acid according to the results of multinuclear NMR spectroscopy. Exposure of this mixture to H_2 results in the clean formation of a new species (**1**). The $^{31}P\{^1H\}$ signals of **1** were observed at $\delta = 35.0$ and 69.7 ppm with a P–P coupling constant of 464 Hz, while the ^{31}P NMR spectrum reveals that the signal at $\delta = 35.0$ ppm also exhibits a P–H coupling of 395 Hz. The corresponding ^1H NMR signal for this P–H fragment appears at $\delta = 5.27$ ppm. In addition a quartet resonance at $\delta = 3.67$ ppm ($^1J_{B-H} = 91$ Hz) was attributed to a B–H fragment. The corresponding ^{11}B and ^{19}F spectra showed resonances at $\delta = -25.3$ ppm and $\delta = -133.1$, -164.0, and -166.9 ppm, respectively, consistent with the presence of the anion $[HB(C_6F_5)_3]$[20] and prompting the formulation of **1** as $[(tBu_2P)PHtBu_2][HB(C_6F_5)_3]$ (Scheme 1). This connectivity was subsequently confirmed by crystallographic data, although disorder within the cation precludes a detailed consideration of the metric parameters.



Scheme 1. Reactions of P_2R_4 affording **1** and **2**.

By employing a similar strategy, $B(C_6F_5)_3$ was added to a mixture of PhC≡CH and P_2Ph_4 in toluene. Subsequent concentration of the mixture afforded colorless crystals of a new species (**2**) in 68% isolated yield. The ^1H NMR spectrum of **2** contained a doublet resonance at $\delta = 8.29$ ppm attributable to an olefinic C–H that exhibited coupling to P of 37 Hz. Compound **2** also gave rise to an upfield ^{11}B resonance at $\delta = -16.1$ ppm and ^{19}F signals attributable to the fluoroarene rings. The corresponding $^{31}P\{^1H\}$ signals were observed at $\delta = 21.4$ and -13.2 ppm with a $^1J_{P-P}$ coupling of 330 Hz. These data support the formulation of **2** as $[(Ph_2P)P(Ph)_2C(Ph)=C(H)B(C_6F_5)_3]$. This notion was subsequently confirmed crystallographically (Figure 1). The structural data affirms that the diphosphine and borane have added to the alkyne affording a zwitterionic species that is best described as an alkenyl-phosphino-phosphonium borate. One of the P centers of the diphosphine adds to the phenyl-sustituted carbon atom of the alkyne, while the borane has added to the unsubstituted end of the alkyne, affording a *trans*-orientation of the B and P about the resulting olefinic C=C bond. The metric parameters about the alkenyl borate are typical of such species. The P–P bond length is 2.2355(8) Å, which is significantly longer than those reported for $[Ph_2PMe(PPh_2)]^+$ (2.187(2) Å) and $[Ph_2PCl(PPh_2)]^+$ (2.205(4) Å),[11f] reflecting the electron-withdrawing nature of the alkenyl-borate substituent in **2**.

Although P_5Ph_5 has been shown to form Lewis acid–base adducts with BH_3,[21] the combination of P_4Cy_4 or P_5Ph_5 with $B(C_6F_5)_3$ results in no apparent interaction with this Lewis

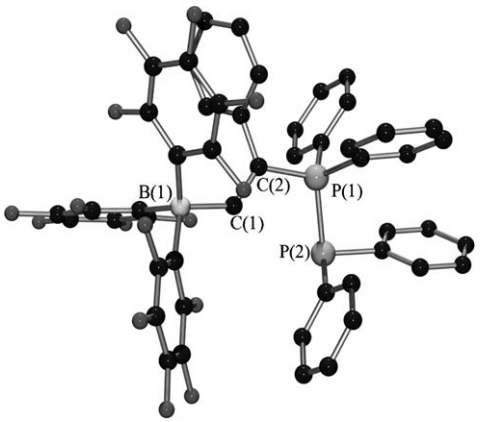
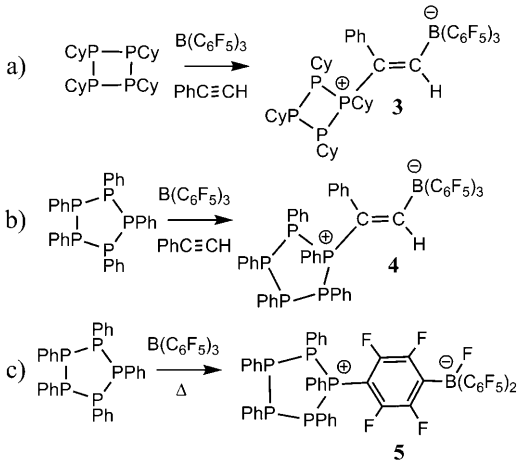


Figure 1. POV-ray drawing of **2**. Selected bond lengths [Å]: B(1)–C(1) 1.642(3), C(1)–C(2) 1.346(3), C(2)–P(1) 1.8069(19), P(1)–P(2) 2.2355(8).

acid by multinuclear NMR spectroscopy between $-60\,^\circ C$ and $40\,^\circ C$. As a result we sought to exploit these systems to effect the conversion to phosphino-phosphonium derivatives.

To this end, PhC≡CH was added to a solution containing $B(C_6F_5)_3$ and P_4Cy_4. A yellow powder was subsequently isolated in 78% yield, which was determined to be the species **3** (Scheme 2b). The ^{31}P NMR spectrum of **3** shows three res-



Scheme 2. Alkyne activation and thermolysis of cyclopolyphosphines and $B(C_6F_5)_3$ affording **3**–**5**.

onances at $\delta = 20.4$, -47.2, and -59.4 ppm, in a ratio of 1:2:1 (Figure 2), characteristic of an AB_2X spin system. The P–P couplings clearly indicated quaternization of a P center giving rise to the downfield resonance. The one-bond P–P coupling constant associated with the cationic P center is roughly double the other one-bond P–P coupling constant (247 Hz, vs. 123 Hz), consistent with the trends noted for $[P_4Ph_4PRR']^+$ ions.[11] The ^{19}F and ^{11}B NMR spectra of **3** are similar to those described for **2**, and thus infer the presence of a borate fragment. Similarly, the ^1H NMR spectrum shows the expected resonances for the cyclohexyl groups as well as a signal attributable to an olefinic C–H with a cou-

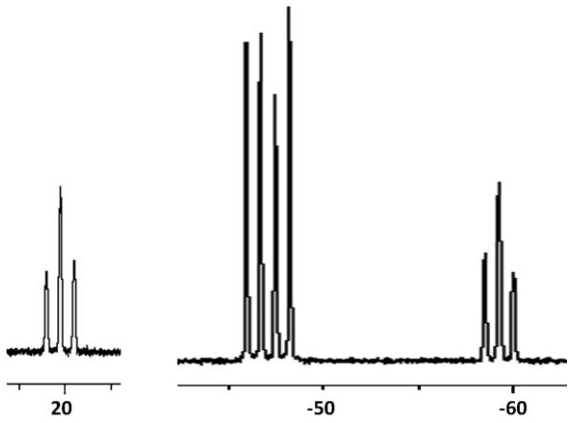


Figure 2. ^{31}P NMR spectrum of **3**.

pling to P of 37 Hz and a phenyl group. These data support the formulation of **3** as the triphosphino-phosphonium borate $[(P_3Cy_3)P(Cy)C(Ph)=C(H)\ B(C_6F_5)_3]$ (Scheme 2). Crystallographic data confirmed this formulation (Figure 3).

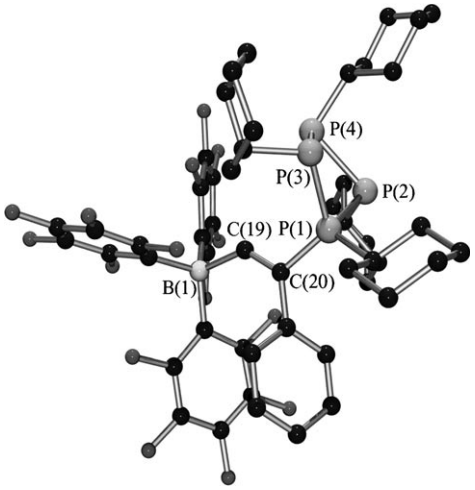


Figure 3. POV-ray drawing of **3**. Selected bond lengths [Å]: B(1)–C(19) 1.647(6), P(1)–C(20) 1.818(4), C(19)–C(20) 1.341(5), P(1)–P(3) 2.1990(15), P(1)–P(2) 2.2106(15), P(2)–P(4) 2.2331(16), P(3)–P(4) 2.2266(16).

The newly formed B–C bond is 1.647(6) Å, while the corresponding P–C bond length is 1.818(4) Å, both of which are typical. The olefinic C=C bond length is also typical at 1.341(5) Å. The P–P bonds of the P_4 ring range from 2.1990(15) to 2.2331(16) Å, similar to that described for **2**.

In an analogous fashion, addition of PhC≡CH to $B(C_6F_5)_3$ and P_5Ph_5 results in the quantitative conversion to a new species (**4**) after 4 h (Scheme 2b). This product exhibited a resonance typical of the olefinic proton in the ^1H NMR spectrum at $\delta = 8.59$ ppm, which exhibits a coupling to P of 42 Hz. A corresponding downfield triplet in the $^{31}P\{^1H\}$ NMR spectrum is observed at $\delta = 20.9$ ppm ($^1J_{P-P} = 300$ Hz). This spectrum also displays multiplet resonances at $\delta = -22.5$, -30.8, -35.6, and -38.9 ppm attributable to four other PPh units; thus, overall there exists a ABCDX spin system. Aside from the resonance attributed to the cationic phosphorus center, the signals in the ^{31}P NMR spectrum were second order and overlapped, typical of related P_5 cations.[11l] The formulation of **4** was unambiguously confirmed by X-ray crystallography to be the zwitterionic tetraphosphino-phosphonium borate addition product $[(Ph_4P_4)P(Ph)C(Ph)=C(H)B(C_6F_5)_3]$ (Figure 4), in which the P_5Ph_5 and $B(C_6F_5)_3$ have added to the alkyne. The B–C, C=

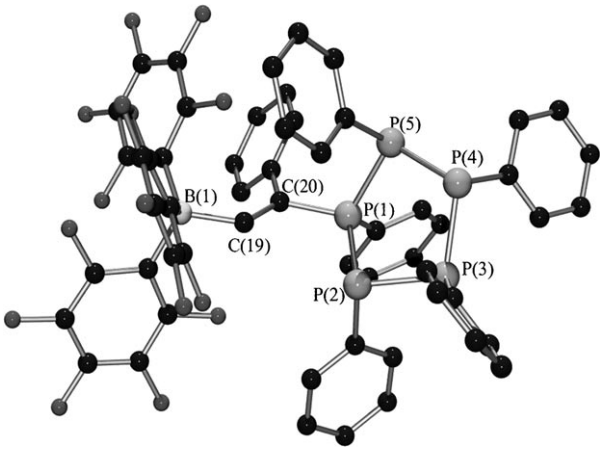


Figure 4. POV-ray drawing of **4**. Selected bond lengths [Å]: B(1)–C(19) 1.640(3), C(19)–C(20) 1.337(3), C(20)–P(1) 1.821(2), P(1)–P(2) 2.2137(8), P(2)–P(3) 2.2190(8), P(3)–P(4) 2.2227(9), P(4)–P(5) 2.2188(8), P(5)–P(1) 2.2077(8).

C, and P–C bond lengths in **4** were similar to those in **2**. The P–P bond lengths lengthen with increasing bonds from the quaternary P center. Thus, the P(1)–P(2) and P(1)–P(5) are comparatively short, averaging 2.2107(8) Å, whereas P(2)–P(3) and P(4)–P(5) average 2.2189(8) Å, and P(3)–P(4) is found to be 2.2227(9) Å. A similar metric trend was described by Burford et al. for the cyclotetraphosphino-phosphonium cation $[(Ph_4P_4)P(Ph)Me]^+$,[11f] although the P–P bonds involving P(1) are somewhat longer in **4**, again as a result of the electron-withdrawing nature of the alkenyl borate substituent.

In the absence of PhC≡CH, the combination of $B(C_6F_5)_3$ and P_5Ph_5 did react under prolonged heating for six days at 120 °C in toluene. This resulted in quantitative formation of the zwitterion $[(Ph_4P_4)P(Ph)C_6F_4B(F)(C_6F_5)_2]$ (**5**) (Scheme 2c). This species, derived from the attack at the *para*-position[14a,15d,22] of one of the fluoroarene rings of $B(C_6F_5)_3$ with concurrent F transfer to B, was isolated in 95% yield.

This structural assignment was supported by observations of a broad signal for the B-F fluorine in the ^{19}F NMR spectrum at $\delta = -193.1$ ppm, a doublet ($^1J_{B-F} = 52$ Hz) in the ^{11}B NMR spectrum at $\delta = -2.7$ ppm, and a downfield triplet in the ^{31}P NMR spectrum at $\delta = 13.3$ ppm ($^1J_{P-P} = 359$ Hz). Similar to **4**, only the resonance attributed to the cationic phosphorus center of this ABDCX spin system is well-resolved in the ^{31}P spectrum of **5**. This resonance is typical of cationic P centers in $[P_4Ph_4PRR']^+$ ions.[11l] This formulation

was further supported by X-ray crystallography (Figure 5). Most of the metric parameters for the borate[15d] and the *tetra*-phosphino-phosphonium.[11l] portions of the molecule were similar to those described above. Similar to **4**, in **5** the

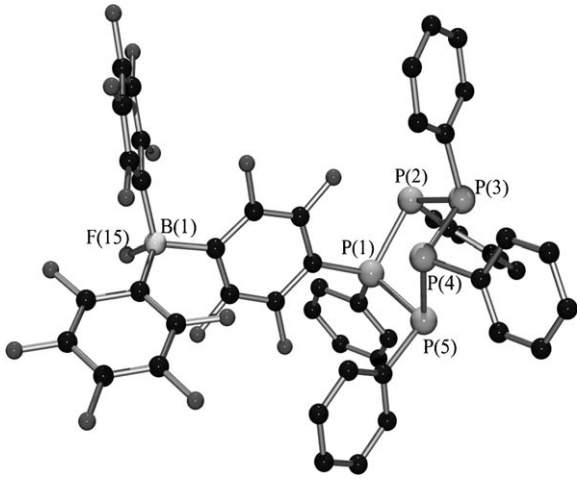


Figure 5. POV-ray drawing of **5**. Selected bond lengths [Å]: B(1)−C(13) 1.661(9), C(16)−P(1) 1.808(6), P(1)−P(2) 2.216(2), P(2)−P(3) 2.242(2), P(3)−P(4) 2.238(2), P(4)−P(5) 2.228(2), P(5)−P(1) 2.200(2), B(1)−F(15) 1.422(8).

P(1)−P(5) and P(1)−P(2) bond lengths of 2.216(2) Å and 2.200(2) Å are significantly longer than those in $[(Ph_4P_4)P(Ph)Me]^+$,[11f] reflecting the electron-withdrawing nature of the fluoroarene substituent. The P_5 ring adopts a pseudo-chair conformation with the phenyl rings on P(1) and P(2) *cis* disposed; the remaining substituents adopt alternating *trans*-dispositions. The phenyl ring on P(5) is oriented approximately parallel to the fluoroarene ring on the cationic P center (P(1)). The distance between these rings reflects some degree of π-stacking of these electron-rich and electron-poor rings.[23] It is noteworthy that the structures of **4** and **5** infer that quaternization of P in the P_5 ring occurs at one of the two P atoms where the Ph groups are disposed in a *cis* orientation. A similar observation was made by Burford et al. for alkylation reactions.[11l]

Conclusions

The above formations of **1**–**5** demonstrate that the steric demands of diphosphines and cyclopolyphosphines can be exploited in frustrated Lewis pair chemistry to achieve H_2 or alkyne activation, and aromatic substitution on a fluroaryl group of the borane. These reactions allow the functionalization of polyphosphines affording cations not available through the use of conventional alkylating agents. As such, these strategies afford new synthetic routes to phosphino-phosphonium salts and zwitterions. The ability to incorporate such functional groups offers the potential for further chemistry of these P−P-bonded systems. We are currently exploring the utility of such polyphosphine derivatives in our laboratory.

Experimental Section

General considerations: All manipulations were performed on a double manifold N_2 (H_2)/vacuum line with Schlenk-type glassware or in an N_2-filled inert atmospheres glove box. The N_2 and H_2 gases were dried by passage through a Dririte column. Solvents (Aldrich) were dried using an Innovative Technologies solvent system (toluene, hexanes, pentane, CH_2Cl_2). NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer and spectra were referenced to residual solvent (^1H, ^{13}C) or externally (^{11}B; BF_3OEt_2; ^{19}F; $CFCl_3$; ^{31}P; 85% H_3PO_4). NMR solvents were purchased from Cambridge Isotopes, dried over CaH_2 (CD_2Cl_2 and $CDCl_3$), vacuum distilled prior to use and stored over 4 Å molecular sieves in the glovebox. tBu$_2$PPtBu$_2$ was generated from reaction of tBu$_2$PLi with tBu$_2$PCl, P_4Cy_4 and P_5Ph_5 were prepared as previously described.[7] P_2Ph_4 was purchased from Aldrich and used as received. B-(C_6F_5)$_3$ was generously donated by NOVA Chemicals Corporation.

Synthesis of [(tBu$_2$P)PHtBu$_2$][HB(C_6F_5)$_3$] (1): B(C_6F_5)$_3$ (50 mg, 0.20 mmol) was added to P_2tBu$_4$ (28 mg, 0.20 mmol) in toluene (2 mL). The pink solution was subjected to three freeze–pump–thaw cycles and backfilled with H_2 at 77 K (ca. 4 atm). The solution was allowed to stir overnight and then pumped to dryness. The solid was washed with pentane (2×2 mL) and again pumped to dryness. Yield: 64 mg (74%). ^1H NMR ($CDCl_3$): δ=1.46 (dd, $^3J_{P-H}$=14 Hz, $^4J_{P-H}$=2 Hz, 18H, C(CH_3)$_3$), 1.57 (dd, $^3J_{P-H}$=15 Hz, $^4J_{P-H}$=1 Hz, 18H, C(CH_3)$_3$), 3.67 (q, $^1J_{B-H}$=91 Hz, 1H, BH), 5.27 ppm (dd, $^1J_{P-H}$=395 Hz, $^2J_{P-H}$=8 Hz, 1H, PH); ^{19}F NMR ($CDCl_3$): δ=−133.1 (br d, $^3J_{F-F}$=23 Hz, 6F, o-C_6F_5), −164.0 (t, $^3J_{F-F}$=20 Hz, 3F, p-C_6F_5), −166.9 ppm (tm, $^3J_{F-F}$=23 Hz, 6F, m-C_6F_5); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=35.0 (d, $^1J_{P-P}$=464 Hz, tBu$_2$$PPHtBu_2$), 69.7 ppm (d, $^1J_{P-P}$=464 Hz, tBu$_2$$PPHtBu_2$); ^{11}B NMR ($CDCl_3$): δ=−25.3 ppm (d, $^1J_{B-H}$=91 Hz); ^{13}C NMR ($CDCl_3$): δ=31.4 (dd, J_{P-C}=15 Hz, J_{P-C}=6 Hz, C(CH_3)$_3$), 32.6 (dd, J_{P-C}=15 Hz, J_{P-C}=7 Hz, C(CH_3)$_3$), 36.8 (dd, J_{P-C}=7 Hz, J_{P-C}=7 Hz, C(CH$_3$)$_3$), 37.2 (dd, J_{P-C}=11 Hz, J_{P-C}=7 Hz, C(CH$_3$)$_3$), 125.2 (br m, B-C), 136.3 (dm, $^1J_{F-C}$=240 Hz, C-F), 137.7 (dm, $^1J_{F-C}$=240 Hz, C-F), 148.3 ppm (dm, $^1J_{F-C}$=240 Hz, C-F); elemental analysis calcd (%) for $C_{34}H_{38}BF_{15}P_2$: C 50.77, H 4.76; found: C 50.34, H 4.68.

Synthesis of E-[(Ph$_2$P)P(Ph)$_2$C(Ph)=C(H)B(C_6F_5)$_3$] (2): A solution of tris(pentafluorophenyl)borane (50 mg, 0.098 mmol) in toluene (5 mL) was added dropwise to a solution of tetraphenylbiphosphine (36 mg, 0.097 mmol) and phenylacetylene (30 mg, 0.29 mmol) in toluene (5 mL). The solution was stirred for 30 min and the volume of the reaction mixture was reduced to 2 mL under reduced pressure. The solution was left at room temperature overnight to afford clear colorless crystals, which were washed with pentane (2×2 mL) and dried in vacuo (65 mg, 68%). ^1H NMR (CD_2Cl_2): δ=6.48 (d, $^3J_{H-H}$=8 Hz, 2H), 6.71 (t, $^3J_{H-H}$=8 Hz, 2H), 6.88 (tm, $^3J_{H-H}$=8 Hz, 1H), 7.16 (t, $^3J_{H-H}$=8 Hz, 4H), 7.25 (tm, $^3J_{H-H}$=8 Hz, 4H), 7.32–7.54 (m, 10H), 7.69 (m, 2H), 8.29 ppm (d, $^3J_{H-P}$=37 Hz, 1H, C=C-H); ^{11}B NMR (CD_2Cl_2): δ=−16.1 ppm (s, br); ^{19}F NMR (CD_2Cl_2): δ=−131.3 (d, 6F, $^3J_{F-F}$=21 Hz, o-C_6F_5), −162.8 (t, 3F, $^3J_{F-F}$=21 Hz, p-C_6F_5), −167.0 ppm (d, 6F, $^3J_{F-F}$=20 Hz, m-C_6F_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ=21.4 (dm, $^1J_{P-P}$=330 Hz, C=C-P(Ph$_2$)-PPh$_2$), −13.2 ppm (d, $^1J_{P-P}$=330 Hz, C=C-PPh$_2$-PPh$_2$); elemental analysis calcd (%) for $C_{47}H_{27}BF_{15}P$: C 60.30, H 2.42; found: C 60.65, H 2.72; X-ray data: $P2_1/c$, a=11.9649(6), b=12.9141(6), c=28.8636(15) Å, β=100.425(3)°, V=4386.3(4) Å^3, Z=4, data: 8802, parameters: 614, $R(>2\sigma)$ 0.0400, wR (all) 0.0931, GOF: 1.007.

Synthesis of E-[(P$_3$Cy$_3$)P(Cy)C(Ph)=C(H)B(C_6F_5)$_3$] (3): To a cold (−35 °C) solution of B(C_6F_5)$_3$ (25 mg, 0.049 mmol) and P_4Cy_4 (22 mg, 0.048 mmol) in CH_2Cl_2 was added phenyl acetylene (20 mg, 0.20 mmol) dropwise. The pale yellow solution was allowed to stir overnight, the solvent was removed in vacuo, and the residue was washed with pentane (1 mL), leaving a yellow powder. Yield: 41 mg (78%). ^1H NMR ($CDCl_3$): δ=1.00 (m, 2H), 1.10–1.37 (m, 18H), 1.55–1.95 (m, 21H), 2.05 (m, 1H),

2.34 (m, 2H), 6.88 (d, $^3J_{H-H}=7$ Hz, 2H, *ortho*-C_6H_5), 7.11 (t, $^3J_{H-H}=7$ Hz, 2H, *m*-C_6H_5), 7.19 (tm, $^3J_{H-H}=7$ Hz, 1H, *para*-C_6H_5), 8.30 ppm (d, $^3J_{P-H}=37$ Hz, C=C-H ^{19}F NMR ($CDCl_3$): $\delta=-130.6$ (d, $^3J_{F-F}=24$ Hz, *o*-C_6F_5), −161.7 (t, $^3J_{F-F}=22$ Hz, *p*-C_6F_5), −165.9 ppm (t, $^3J_{F-F}=23$ Hz, *m*-C_6F_5); ^{31}P NMR ($CDCl_3$): $\delta=20.4$ (t, $^1J_{P-P}=247$ Hz), −47.2 (dd, $^1J_{P-P}=247$ Hz, $J=123$ Hz, 2P), −59.4 ppm (t, $J=123$ Hz, 1P); ^{11}B NMR ($CDCl_3$): $\delta=-15.9$ ppm (br s); elemental analysis calcd (%) for $C_{50}H_{50}BF_{15}P_4$: C 56.09, H 4.71; found: C 56.26, H 4.94; X-ray data: *P*21/*n*, $a=15.6548(11)$, $b=16.7208(10)$, $c=19.0352(13)$ Å, $\beta=100.341(2)°$, $V=4901.7(5)$ Å^3, $Z=4$, data: 11237, parameters: 631, $R(>2\sigma)$ 0.0719, *wR* (all) 0.1375, GOF: 0.968.

Synthesis of *E*-[(Ph$_4$P$_4$)P(Ph)C(Ph)=C(H)B(C$_6$F$_5$)$_3$] (4): To a solution of $B(C_6F_5)_3$ (55 mg, 0.11 mmol) and P_5Ph_5 (50 mg, 0.093 mmol) in CH_2Cl_2 was added phenyl acetylene (20 mg, 0.20 mmol). The pale yellow solution was allowed to stir overnight, the solvent was removed in vacuo, and the residue was washed with pentane (2×2 mL), leaving an off-white powder. Yield: 105 mg (91%). X-ray quality crystals were grown from a layered solution of $CDCl_3$/pentane. ^{1}H NMR (CD_2Cl_2): $\delta=5.98$ (d, $J=9$ Hz, 2H), 6.51 (t, $J=8$ Hz, 2H), 6.76 (t, $J=8$ Hz, 1H), 7.01–7.74 (m, 25H), 8.59 ppm (dd, $^3J_{P-H}=42$ Hz, $J=4$ Hz, 1H, C=C-H); ^{19}F NMR (CD_2Cl_2): −131.0 (d, $^3J_{F-F}=24$ Hz, *o*-C_6F_5), −163.1 (t, $^3J_{F-F}=22$ Hz, *p*-C_6F_5), −167.3 ppm (t, $^3J_{F-F}=19$ Hz, *m*-C_6F_5); ^{31}P NMR (CD_2Cl_2): $\delta=20.9$ (t, $^1J_{P-P}=300$ Hz), −22.5 (m, 1P), −30.8 (m, 1P), −35.6–38.9 ppm (m, 2P); ^{11}B NMR (CD_2Cl_2): $\delta=-15.5$ ppm (br s);elemental analysis calcd (%) for $C_{56}H_{31}BF_{15}P_5$: C 58.26, H 2.71; found: C 58.37, H 2.94; X-ray data: $P\bar{1}$, $a=12.8543(9)$, $b=12.9762(10)$, $c=18.0053(12)$ Å, $\alpha=74.201(4)$, $\beta=76.183(4)$, $\gamma=61.367(4)°$, $V=2515.5(3)$ Å^3, $Z=2$, data: 11491, parameters: 694, $R(>2\sigma)$ 0.0449, *wR* (all) 0.1072, GOF: 1.024.

Synthesis *E*-[(Ph$_4$P$_4$)P(Ph)C$_6$F$_4$B(F)(C$_6$F$_5$)$_2$] (5): P_5Ph_5 (300 mg, 0.55 mmol) was added to a solution of $B(C_6F_5)_3$ (283 mg, 0.55 mmol) in toluene (20 mL). The solution was heated at 120°C for six days. Volatiles were removed in vacuo and the residue was washed with hexanes (2× 5 mL). Yield: 554 mg (95%). X-ray quality crystals were grown from a layered solution of CH_2Cl_2/C_6H_6/pentane. ^{1}H NMR (CD_2Cl_2): $\delta=7.12$–7.55 (m, 18H), 7.63 (t, $^3J_{H-H}=7$ Hz, 1H), 7.74 (t, $^3J_{H-H}=8$ Hz, 2H), 7.87 (t, $^3J_{H-H}=7$ Hz, 2H), 7.94 ppm (t, $^3J_{H-H}=8$ Hz, 2H ^{19}F NMR (CD_2Cl_2): $\delta=-127.6$ (d, $^3J_{F-P}=68$ Hz, 2F, C_6F_4), −130.3 (s, 2F, C_6F_4), −135.4 (m, *o*-C_6F_5), −161.9 (t, $^3J_{F-F}=20$ Hz, *p*-C_6F_5), −166.9 (m, *m*-C_6F_5), −193.1 ppm (br s, B-F); ^{31}P NMR (CD_2Cl_2): $\delta=13.3$ (tm, $^1J_{P-P}=359$ Hz, 1P), −19.3 (ddm, $^1J_{P-P}=359$ Hz, 78 Hz, 1P), −28.8 (dd, $J=343$ Hz, 107 Hz, 1P), −37.8 ppm (m, 2P); ^{11}B NMR (CD_2Cl_2): $\delta=-2.7$ (d, $^1J_{B-F}=52$ Hz). Despite repeated attempts, satisfactory elemental analysis data could not be obtained for this compound. X-ray data: *C*2/*c*, $a=35.645(4)$, $b=15.6446(15)$, $c=25.300(3)$ Å, $\beta=134.5620(10)°$, $V=10052.2(17)$ Å^3, $Z=8$, data: 8858, parameters: 622, $R(>2\sigma)$ 0.0765, *wR* (all) 0.2695, GOF: 1.047.

X-ray data collection and reduction: 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 with $Mo_{K\alpha}$ radiation ($\lambda=0.71069$ A°). The data were collected at 150(±2) K for (**1**–**4**), data for **5** was collected at 296 K. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multi-scan method (SADABS).

Structure solution and refinement: Non-hydrogen atomic scattering factors were taken from the literature tabulations.[24] The heavy atom positions were determined by 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 $\omega(F_o-F_c)^2$, where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all 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 atom to which they are bonded, assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 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. Additional details are provided in the Supporting Information.

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