VIP **Addition Reactions**

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Reactivity of “Frustrated Lewis Pairs”: Three-Component Reactions of Phosphines, a Borane, and Olefins**

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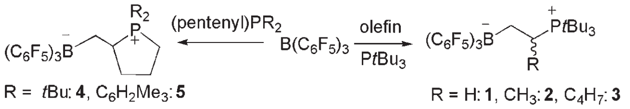
The formation of Lewis acid/base adducts is a classical concept in chemistry.[1] This principle is fundamental to main-group chemistry, the basis of the coordination chemistry of transition metals,[2] and the foundation of a variety of both stoichiometric and catalytic organic transformations.[3] In all of these cases, the observed chemistry is predicated on the interaction of a Lewis base with a Lewis acid in a donor–acceptor fashion. In our recent studies, we have been studying systems in which steric demands preclude such classical donor–acceptor interactions. Such “frustrated Lewis pairs” lead to unique and unprecedented reactivity. For example, we have reported that the reaction of $B(C_6F_5)_3$ with the sterically demanding secondary phosphine $(C_6H_2Me_3)_2PH$ results in *para* attack to afford species of the form $(C_6H_2Me_3)_2PH(C_6F_4)BF(C_6F_5)_2$, which is readily converted into $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$.[4,5] This latter species was shown to reversibly liberate and take-up H_2.[6] Such *para* substitutions have been exploited to tune Lewis acidity, thereby providing ready access to the boranes $R_2P(C_6F_4)B(C_6F_5)_2$ (R = *t*Bu, $C_6H_2Me_3$) and the cationic boranes $[R'R_2P(C_6F_4)B(C_6F_5)_2]^+$ (R′ = H, R = *t*Bu, $C_6H_2Me_3$, R′ = R = *i*Pr, cyclohexyl).[7] No reaction between the Lewis acid and Lewis base were apparent for related phosphine/borane combinations in which steric demands are even greater. Nonetheless, such sterically “frustrated Lewis pairs” effect the heterolytic cleavage of H_2 to give the salts $[R_3PH][HB(C_6F_5)_3]$ (R = *t*Bu, $C_6H_2Me_3$).[8] Herein, we broaden the reactivity of “frustrated Lewis pairs” and demonstrate that sterically demanding phosphines and boranes react with olefins to give alkanediyl-linked phosphonium borates. These three-component reactions are surprising given that neither tertiary phosphines nor tertiary boranes are known to react with olefins.

A solution of bromobenzene containing the combination of tBu_3P and $B(C_6F_5)_3$ was purged with ethylene and stored under 1 atm of ethylene at 25 °C. Over the course of several hours, a colorless precipitiate of **1** formed which was isolated in 63 % yield by filtration. The $^{31}P\{^1H\}$ NMR spectrum of **1** showed a singlet resonance at $\delta = 50.1$ ppm while the corresponding $^{11}B\{^1H\}$ NMR signal was observed at $\delta = -13.3$ ppm. The ^1H NMR spectrum of **1** showed broad multiplets at $\delta = 1.69$–1.94 ppm. These data confirm the presence of phosphonium and borate fragments linked by C_2H_4, thus affirming the formulation of **1** as $[tBu_3P(C_2H_4)B(C_6F_5)_3]$ (Scheme 1). An X-ray crystallographic study (Figure 1 a)[9] confirmed the proposed zwitterionic formulation,



Scheme 1. Inter- and intramolecular addition of frustrated phosphine/borane pairs to olefins.

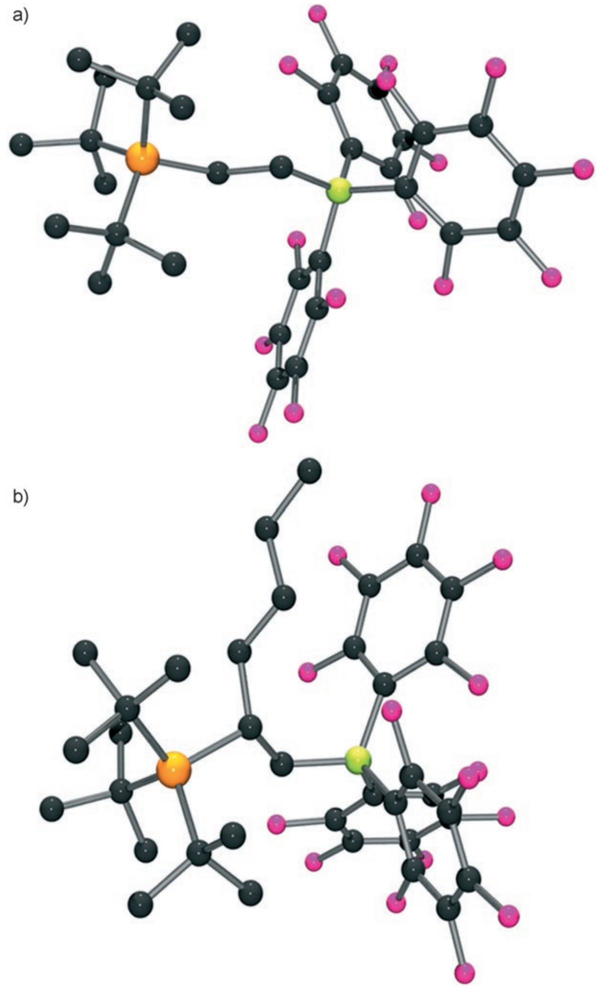


Figure 1. POV-ray drawings of a) **1** and b) **3**. Hydrogen atoms are omitted for clarity. C: black, P: orange, F: pink, B: yellow-green.

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thus establishing unambiguously that the phosphine and borane add to opposite ends of the ethylene molecule with the formation of pseudotetrahedral centers in both cases. The B−C and P−C bond lengths were found to be 1.653(4) Å and 1.831(3) Å, respectively, which are unexceptional. The remarkably facile formation of **1** stands in contrast to the more conventional syntheses of the related phosphine–borane species $Ph_2PCH{=}CHB(C_6H_2Me_3)_2$ and $Ph_2PCH_2CH_2B(C_6H_2Me_3)_2$ previously reported by Marder and co-workers.[10,11]

Similar intermolecular reactions of propylene and 1-hexene with $t\mathrm{Bu}_3\mathrm{P}$ and $B(C_6F_5)_3$ afforded the new species **2** and **3** which were subsequently isolated in yields of 63 and 55%. These products exhibited $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR signals at $\delta = 56.9$ and -11.6, and 58.3 and -13.0 ppm, respectively, which are consistent with the presence of phosphonium and borate fragments similar to those found in **1**. The ^1H and ^{19}F NMR spectra reveal the expected resonances for propyl and hexyl groups as well as inequivalent C_6F_5 groups, which is consistent with the generation of a chiral center from the prochiral olefins. Two-dimensional ^{13}C-^1H NMR correlation spectra were used to establish resonance assignments. These data supported a regiochemistry of addition in which the P atom adds to the secondary olefinic carbon atom while the B atom adds to the terminal methylene group, thus prompting the formulations of **2** and **3** as $[t\mathrm{Bu}_3\mathrm{P}(\mathrm{CH(R)CH_2B}(C_6F_5)_3]$, where $R = CH_3$ and C_4H_9, respectively. An X-ray crystallographic study of **3** confirmed this regiochemistry of addition (Figure 1 b).[9]

These "frustrated Lewis pairs" can also react with olefins in an intramolecular fashion. The olefinic derivatives of sterically demanding phosphines of the form $CH_2{=}CH(CH_2)_3PR_2$ ($R = t\mathrm{Bu}$, $C_6H_2Me_3$) were prepared by conventional methods. Stoichiometric reactions with $B(C_6F_5)_3$ were monitored by ^{31}P NMR spectroscopy, which revealed no evidence for the formation of phosphine–borane adducts. Rather, the reaction proceeds in CH_2Cl_2 at 25–45 °C to give species **4** and **5** in 94 and 52% yields, respectively. The $^{31}P\{^1H\}$ NMR spectra of **4** and **5** showed singlet resonances at $\delta = 62.4$ and 52.8 ppm, while the corresponding $^{11}B\{^1H\}$ NMR signals were observed at $\delta = -13.8$ and -13.7 ppm, respectively. The ^{19}F NMR spectra for **4** and **5** confirmed the presence of C_6F_5 groups. These data together with the ^1H and ^{13}C NMR data support the formulation of **4** and **5** as the cyclized phosphonium borates $[R_2PCH(C_3H_6)CH_2B(C_6F_5)_3]$, with $R = t\mathrm{Bu}$ (**4**) and $R = C_6H_2Me_3$ (**5**; Scheme 1). An X-ray crystallographic study of **4** (Figure 2)[9] confirmed the proposed connectivity, although rotational disorder of the *tert*-butyl groups dictated a constrained refinement. Related addition of P−H bonds to a pendant olefinic group mediated by a lanthanide species have been proposed as catalytic hydrophosphination intermediates en route to the secondary phospholes $HPCH(Me)(C_3H_6)$.[12,13]

The mechanism of the present reactions is intriguing given that these phosphines and boranes are not known to react individually with olefins. It is tempting to suggest that these reactions are initiated by activation of the olefin by the Lewis acid, which prompts attack by the phosphine. This view is supported to some degree by the observations of Herrebout and van der Veken,[14] who reported IR data for the van der Waals BF_3–ethylene and BF_3–propylene complexes generated in an argon matrix at 93–125 K. We attempted to observe an analogous borane–olefin interaction by variable-temperature NMR methods using solutions of $B(C_6F_5)_3$ in 1-hexene. No evidence of interaction was observed by ^{19}F, ^{11}B, or ^1H NMR spectroscopy at temperatures down to −90 °C. It is noteworthy that DFT calculations for ethylene–alane[15] and ethylene–borane adducts[16] suggested that weak π-donation complexes are formed. In the case of the olefin–BF_3 adduct, only small deviations in the geometry of the olefin and the borane were computed upon complexation,[16] which suggests that in the present cases the phosphine nucleophile may play a significant role in driving the addition reaction. It is noteworthy that conventional hydroboration is postulated to proceed via a π-olefin–borane complex.[17] These additions of B and P groups across olefins are also reminiscent of Br_2 addition to olefins, as the latter is proposed to proceed by the attack of an electrophilic bromonium ion (Br^+, Lewis acid) followed by a nucleophilic attack of a bromide ion (Br^-, Lewis base).[17]

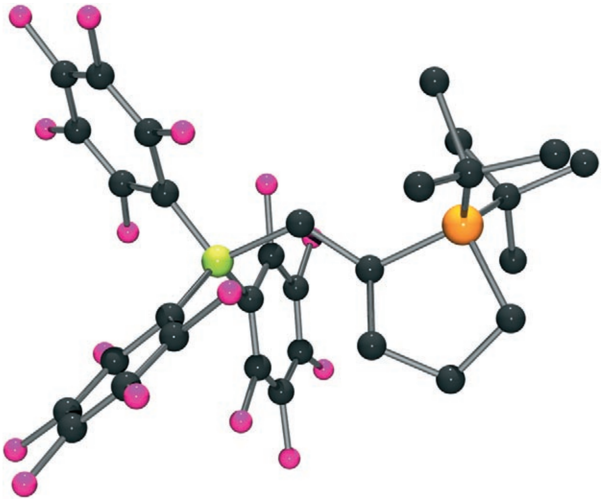

Figure 2. POV-ray drawing of **4**. Hydrogen atoms are omitted for clarity. C: black, P: orange, F: pink, B: yellow-green.

In summary, sterically frustrated Lewis pairs of phosphines and the borane $B(C_6F_5)_3$ exhibit unprecedented reactivity with olefins, and undergo both intermolecular additions as well as intramolecular cyclizations. These reactions are all the more remarkable given that any pair of these reagents do not react, but the combination of the three reagents results in formation of the product. The utility of such remarkably selective three-component reactions and the further reactivity of "frustrated Lewis pairs" are the subject of ongoing study.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free N_2 by employing both Schlenk-line techniques and an Innovative Technologies or Vacuum Atmospheres inert-atmosphere glove box. Solvents were purified by employing a Grubbs-type column system manufactured by Innovative Technology. ^1H, ^{13}C, ^{11}B, ^{19}F, and

^{31}P NMR spectroscopy spectra were recorded on a Bruker Avance-300 spectrometer. ^{1}H and ^{13}C NMR spectra are referenced to $\mathrm{SiMe_4}$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B, and ^{19}F NMR spectroscopy were referenced to 85 % $\mathrm{H_3PO_4}$, $\mathrm{BF_3}$, and $\mathrm{CFCl_3}$, respectively. For experimental details see the Supporting Information. [D$_8$]THF was used as the solvent for the NMR analyses of **1**–**3** and $\mathrm{CD_2Cl_2}$ for **4** and **5.** Combustion analyses were performed in house on a Perkin Elmer CHN analyzer. $\mathrm{B(C_6F_5)_3}$ was generously donated by NOVA Chemicals Corporation.

1: A solution of *t*Bu$_3$P (0.221 g, 1.09 mmol) in $\mathrm{C_6H_5Br}$ (2 mL) was added to a solution of $\mathrm{B(C_6F_5)_3}$ (0.499 g, 0.97 mmol) in $\mathrm{C_6H_5Br}$ (50 mL) under an ethylene purge. The solution was purged with ethylene for 1 h and then the reaction was stirred under 1 atm of ethylene at room temperature for 16 h. The solvent was removed in vacuo and the residue was dissolved in $\mathrm{CH_2Cl_2}$. Hexanes were then added to precipitate a white solid, which was isolated by filtration and washed with hexanes several times before being dried in vacuo. Yield: 0.452 g (63 %). Crystals suitable for X-ray diffraction were grown from a layered $\mathrm{CH_2Cl_2}$/pentane solution at 25 °C. H NMR: $\delta = 1.69$–1.94 (br m, 4 H, $\mathrm{C_2H_4}$), 1.43 ppm (d, 27 H, $^{3}J_{\mathrm{H\text{-}P}} = 14$ Hz, *t*Bu); ^{11}B{^{1}H} NMR: $\delta = -13.3$ ppm; ^{13}C{^{1}H} NMR partial: $\delta = 149.17$ (dm, $^{1}J_{\mathrm{C\text{-}F}} = 238$ Hz, *o*-$\mathrm{C_6F_5}$), 139.06 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 244$ Hz, *p*-$\mathrm{C_6F_5}$), 137.57 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 245$ Hz, *m*-$\mathrm{C_6F_5}$), 39.92 (d, $^{1}J_{\mathrm{C\text{-}P}} = 30$ Hz, *t*Bu), 29.90 (s, *t*Bu), 19.00 (d, $^{1}J_{\mathrm{C\text{-}P}} = 30$ Hz, $\mathrm{PCH_2}$), 17.63 ppm (br s, $\mathrm{BCH_2}$); ^{19}F NMR: $\delta = -132.58$ (d, 6 F, $^{3}J_{\mathrm{F\text{-}F}} = 25$ Hz, *o*-$\mathrm{C_6F_5}$), -164.14 (t, 3 F, $^{3}J_{\mathrm{F\text{-}F}} = 20$ Hz, *p*-$\mathrm{C_6F_5}$), -167.27 ppm (t, 6 F, $^{3}J_{\mathrm{F\text{-}F}} = 20$ Hz, *m*-$\mathrm{C_6F_5}$); ^{31}P{^{1}H} NMR: 50.0 ppm. Elemental analysis calcd for $\mathrm{C_{32}H_{31}BF_{15}P}$: C 51.77, H 4.21; found: C 51.92, H 3.93 %.

2: A solution of *t*Bu$_3$P (0.258 g, 1.28 mmol) in $\mathrm{C_6H_5Br}$ (2 mL) was added to a solution of $\mathrm{B(C_6F_5)_3}$ (0.473 g, 0.92 mmol) in $\mathrm{C_6H_5Br}$ (50 mL) under a propylene purge. The solution was purged with propylene for 4 h and then the reaction was stirred under 1 atm of propylene at room temperature for 12 h. The solvent was removed in vacuo and the residue was dissolved in $\mathrm{CH_2Cl_2}$. Hexanes were then added to precipitate a white solid, which was isolated by filtration and washed with hexane several times before being dried in vacuo. Yield: 0.436 g (63 %). ^{1}H NMR: $\delta = 2.72$ (br s, 1 H, PCH), 2.30 (br s, 2 H, $\mathrm{BCH_2}$), 1.59 (d, 27 H, $^{3}J_{\mathrm{H\text{-}P}} = 13$ Hz, *t*Bu), 1.57 ppm (m, 3 H, Me); ^{11}B{^{1}H} NMR: $\delta = -11.6$ ppm; ^{13}C{^{1}H} NMR partial: $\delta = 149.18$ (dm, $^{1}J_{\mathrm{C\text{-}F}} = 237$ Hz, *o*-$\mathrm{C_6F_5}$), 139.13 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 230$ Hz, *p*-$\mathrm{C_6F_5}$), 137.57 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 245$ Hz, *m*-$\mathrm{C_6F_5}$), 41.62 (d, $^{1}J_{\mathrm{C\text{-}P}} = 25$ Hz, *t*Bu), 33.74 (d, $^{1}J_{\mathrm{C\text{-}P}} = 22$ Hz, PCH), 31.15 (s, *t*Bu), 18.92 ppm (s, Me); ^{19}F NMR: $\delta = -129.08$ (br s, 6 F, *o*-$\mathrm{C_6F_5}$), -162.41 (t, 3 F, $^{3}J_{\mathrm{F\text{-}F}} = 20$ Hz, *p*-$\mathrm{C_6F_5}$), -165.53 ppm (mt, 6 F, *m*-$\mathrm{C_6F_5}$); ^{31}P{^{1}H} NMR: 56.9 ppm. Elemental analysis calcd for $\mathrm{C_{33}H_{33}BF_{15}P}$: C 52.40, H 4.40; found: C 52.14, H 4.36 %.

3: A solution of *t*Bu$_3$P (0.211 g, 1.04 mmol) in 1-hexene (2 mL) was added to a solution of $\mathrm{B(C_6F_5)_3}$ (0.496 g, 0.97 mmol) in 1-hexene (30 mL). The solution was stirred at room temperature for 12 h, during which time a white precipitate formed. The solid was isolated by filtration and washed with pentanes and dried in vacuo. Yield: 0.428 g (55 %). Crystals suitable for X-ray diffraction were grown from a layered $\mathrm{CH_2Cl_2}$/pentane/$\mathrm{C_6D_6}$ solution at 25 °C. ^{1}H NMR: $\delta =$ 2.84 (br m, 1 H, P-CH), 2.40 (br m, 1 H, $\mathrm{CHC}H_2$), 2.12 (br m, 2 H, $\mathrm{BCH_2}$), 1.63 (d, 27 H, $^{3}J_{\mathrm{H\text{-}P}} = 13$ Hz, *t*Bu), 1.53 (br m, 1 H, $\mathrm{CHC}H_2$), 1.02–1.34 (br m, 2 H, $\mathrm{CH_2}CH_2\mathrm{CH_2}$), 0.78–0.93 (m, 2 H, $\mathrm{CH_2}Me$), 0.69 ppm (t, 3 H, $^{3}J_{\mathrm{H\text{-}H}} = 7$ Hz, Me); ^{1}B{^{1}H} NMR: $\delta = -13.0$ ppm; ^{13}C{^{1}H} NMR partial: $\delta = 149.51$ (dm, $^{1}J_{\mathrm{C\text{-}F}} = 237$ Hz, *o*-$\mathrm{C_6F_5}$), 139.28 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 244$ Hz, *p*-$\mathrm{C_6F_5}$), 137.81 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 256$ Hz, *m*-$\mathrm{C_6F_5}$), 42.18 (d, $^{1}J_{\mathrm{C\text{-}P}} = 24$ Hz, *t*Bu), 40.19 (d, $^{1}J_{\mathrm{C\text{-}P}} = 18$ Hz, P*C*H), 33.90 (s, $\mathrm{CH}C\mathrm{H_2}$), 33.11 (d, $^{3}J_{\mathrm{C\text{-}P}} = 10$ Hz, $\mathrm{CH_2}C\mathrm{H_2CH_2}$), 31.58 (s, *t*Bu), 23.99 (s, $C\mathrm{H_2Me}$), 14.01 ppm (s, Me); ^{19}F NMR: $\delta = -129.31$ (br s, 2 F, *o*-$\mathrm{C_6F_5}$), -130.66 (br s, 4 F, *o*-$\mathrm{C_6F_5}$), -164.22 (t, 3 F, $^{3}J_{\mathrm{F\text{-}F}} = 20$ Hz, *p*-$\mathrm{C_6F_5}$), -167.42 ppm (t, 6 F, $^{3}J_{\mathrm{F\text{-}F}} = 23$ Hz, *m*-$\mathrm{C_6F_5}$); ^{31}P{^{1}H} NMR: $\delta =$ 58.3 ppm. Elemetal analysis calcd for $\mathrm{C_{36}H_{39}BF_{15}P}$: C 54.15, H 4.92; found: C 53.93, H 4.64 %.

4: *t*Bu$_2$$\mathrm{PCH_2CH_2CH_2CH{=}CH_2}$ (0.314 g,1.47 mmol) was added to a solution of $\mathrm{B(C_6F_5)_3}$ (0.704 g, 1.37 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL). The solution was stirred overnight and the solvent removed in vacuo. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (3 mL) and then pentane was added to precipitate a white solid, which was isolated by filtration and washed with pentanes several times. Yield 0.932 g (94 %). ^{1}H NMR: $\delta = 2.78$ (br m, 1 H, CH), 1.95–2.30 (br m, 6 H, $\mathrm{BCH_2}$, $\mathrm{CH_2}CH_2$), 1.37 (d, 9 H, $^{3}J_{\mathrm{H\text{-}P}} = 15$ Hz, *t*Bu), 1.41–1.53 (br m, 2 H, $\mathrm{PCH_2}$), 1.22 ppm (d, 9 H, $^{3}J_{\mathrm{H\text{-}P}} = 15$ Hz, *t*Bu); ^{11}B{^{1}H} NMR: $\delta = -13.8$ ppm; ^{13}C{^{1}H} NMR partial: $\delta = 148.81$ (dm, $^{1}J_{\mathrm{C\text{-}F}} = 234$ Hz, *o*-$\mathrm{C_6F_5}$), 138.70 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 245$ Hz, *p*-$\mathrm{C_6F_5}$), 137.45 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 233$ Hz, *m*-$\mathrm{C_6F_5}$), 40.29 (d, $^{1}J_{\mathrm{C\text{-}P}} = 32$ Hz, P*C*H), 36.27 (d, $^{1}J_{\mathrm{C\text{-}P}} = 29$ Hz, *t*Bu), 34.89 (d, $^{1}J_{\mathrm{C\text{-}P}} = 32$ Hz, *t*Bu), 33.29 (s, $C\mathrm{H_2CH}$), 28.16 (s, *t*Bu), 27.38 (s, *t*Bu), 25.89 (s, $\mathrm{PCH_2}C\mathrm{H_2}$), 18.79 ppm (d, $^{1}J_{\mathrm{C\text{-}P}} = 44$ Hz, $\mathrm{P}C\mathrm{H_2}$); ^{19}F NMR: $\delta = -131.71$ (d, 6 F, $^{3}J_{\mathrm{F\text{-}F}} = 23$ Hz, *o*-$\mathrm{C_6F_5}$), -163.24 (t, 3 F, $^{3}J_{\mathrm{F\text{-}F}} = 20$ Hz, *p*-$\mathrm{C_6F_5}$), -166.73 ppm (t, 6 F, $^{3}J_{\mathrm{F\text{-}F}} = 20$ Hz, *m*-$\mathrm{C_6F_5}$); ^{31}P{^{1}H} NMR: $\delta = 62.4$ ppm. Elemental analysis calcd for $\mathrm{C_{31}H_{27}BF_{15}P}$: C 51.26, H 3.75; found: C 51.26, H 3.64 %.

5: $\mathrm{(2,4,6\text{-}MeC_6H_2)_2PCH_2CH_2CH_2CH{=}CH_2}$ (0.095 g, 0.28 mmol) was added to a solution of $\mathrm{B(C_6F_5)_3}$ (0.155 g, 0.30 mmol) in $\mathrm{CH_2Cl_2}$ (30 mL) and the solution refluxed for 72 h. The solvent was removed in vacuo and the residue was dissolved in $\mathrm{CH_2Cl_2}$ (3 mL) and then pentane was added to precipitate a white solid. The solid was filtered and washed with pentanes several times. Yield 0.124 g (52 %). ^{1}H NMR: $\delta = 6.90$–6.98 (br m, 4 H, $\mathrm{C_6H_2}$), 3.50 (m, 1 H, $\mathrm{PCH_2}$), 3.32 (br m, 1 H, CH), 2.32–2.43 (br m, 3 H, $\mathrm{PCH_2CH_2}$), 2.30 (s, 3 H, Me-4), 2.25 (s, 3 H, Me-4), 1.85–2.22 ppm (br m, 16 H, 2,6-Me, $\mathrm{BCH_2}$, $CH_2\mathrm{CH}$); ^{11}B{^{1}H} NMR: $\delta = -13.7$ ppm; ^{13}C{^{1}H} NMR partial: $\delta =$ 148.64 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 245$ Hz, *o*-$\mathrm{C_6F_5}$), 145.04 (s, *o*-$\mathrm{C_6H_2}$), 145.00 (s, *o*-$\mathrm{C_6H_2}$), 144.53 (s, *o*-$\mathrm{C_6H_2}$), 144.51 (s, *o*-$\mathrm{C_6H_2}$), 141.99 (s, *p*-$\mathrm{C_6H_2}$), 141.86 (s, *p*-$\mathrm{C_6H_2}$), 138.60 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 243$ Hz, *p*-$\mathrm{C_6F_5}$), 137.20 (dm, $^{1}J_{\mathrm{C\text{-}F}} = 257$ Hz, *m*-$\mathrm{C_6F_5}$), 133.07 (s, *m*-$\mathrm{C_6H_2}$), 132.93 (s, *m*-$\mathrm{C_6H_2}$), 132.42 (s, *m*-$\mathrm{C_6H_2}$), 132.27 (s, *m*-$\mathrm{C_6H_2}$), 41.78 (d, $^{1}J_{\mathrm{C\text{-}P}} = 33$ Hz, *C*H), 32.16 (d, $^{1}J_{\mathrm{C\text{-}P}} = 22$ Hz, $\mathrm{P}C\mathrm{H_2}$), 30.75 (d, $^{2}J_{\mathrm{C\text{-}P}} = 10$ Hz, $C\mathrm{H_2CH}$), 24.35 (d, $^{2}J_{\mathrm{C\text{-}P}} = 10$ Hz, $\mathrm{PCH_2}C\mathrm{H_2}$), 22.99 (s, 2,6-Me), 22.94 (s, 2,6-Me), 21.38 (s, 4-Me), 21.19 ppm (s, 4-Me); ^{19}F NMR: $\delta = -132.02$ (d, 6 F, $^{3}J_{\mathrm{F\text{-}F}} = 20$ Hz, *o*-$\mathrm{C_6F_5}$), -163.47 (t, 3 F, $^{3}J_{\mathrm{F\text{-}F}} = 25$ Hz, *p*-$\mathrm{C_6F_5}$), -166.86 ppm (t, 6 F, $^{3}J_{\mathrm{F\text{-}F}} = 20$ Hz, *m*-$\mathrm{C_6F_5}$); ^{31}P{^{1}H} NMR: $\delta = 52.8$ ppm. Elemental analysis calcd for $\mathrm{C_{41}H_{31}BF_{15}P}$: C 57.9, H 3.67; found: C 57.63, H 3.63 %.

Preparative details for $\mathrm{CH_2{=}CH(CH_2)_3PR_2}$ (R = *t*Bu, $\mathrm{C_6H_2Me_3}$) are deposited in the Supporting Information. CCDC-639620–639622 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[9] X-ray data: **1**: monoclinic, space group $P2_1/c$, $a = 11.9532(14)$, $b = 15.3319(18)$, $c = 18.729(2)$ Å, $\beta = 107.436(2)°$, $V = 3274.7(7)$ Å^3. Data: 5758, parameters = 458, $R = 0.0452$, $R_w = 0.1046$, GOF = 1.017. **3**: monoclinic, space group $P\bar{1}$, a = 11.352(4), $b = 11.609(4)$, $c = 15.623(5)$ Å, $\alpha = 111.445(4)$, $\beta = 99.753(4)$, $\gamma = 93.350(4)°$, $V = 1872.4(11)$ Å^3. Data: 6576, parameters = 507, $R = 0.0556$, $R_w = 0.1515$, GOF = 1.005. **4**: monoclinic, space group Pc, $a = 14.994(3)$, $b = 12.770(2)$, $c = 16.538(3)$ Å, $\beta = 94.449(3)°$, $V = 3157.1(9)$ Å^3. Data: 11111, parameters: 865, $R = 0.0838$, $R_w = 0.1933$, GOF = 1.002.

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