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# Phosphinimine–borane combinations in frustrated Lewis pair chemistry†

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The phosphinimines  $Ph_3PNR$  (R = Ph 1,  $C_6F_5$  2, tBu 3) are combined with  $B(C_6F_5)_3$  in an effort to explore the frustrated Lewis pair (FLP) chemistry. While compound 1 is shown to form an adduct with the borane, compounds 2 and 3 exhibit no apparent interaction. Nonetheless exposure of each of the three combinations to  $H_2$  resulted in the formation of the corresponding salts  $[Ph_3PN(H)R][HB(C_6F_5)_3]$  (R = Ph 5,  $C_6F_5$  6, tBu 7). Reaction of 1 or 2 with  $B(C_6F_5)_3$  and carbon dioxide afforded  $Ph_3PN(R)COOB(C_6F_5)_3$  (R = Ph 8,  $C_6F_5$  9) while the corresponding reaction with 3 gave rise only to the tBuNCO and  $(Ph_3PO)B(C_6F_5)_3$ . Reactions of 1–3 and  $B(C_6F_5)_3$  with PhC=CH proceeds to give either deprotonation or addition affording products of the form  $[Ph_3PN(H)R][PhC=CB(C_6F_5)_3]$  or  $(Ph_3PNR)(Ph)C=CH(B(C_6F_5)_3)$ . The factors governing the nature of the dominant products are considered.

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# Introduction

The advent of frustrated Lewis pairs (FLPs) in 2006 has resulted in a new strategy for the activation of small molecules.<sup>1-5</sup> The initial approach was based on the combination of a sterically encumbered Lewis acid and base.<sup>6,7</sup> The notion was that steric demands that preclude adduct formation could then be exploited for further chemistry. Subsequently it was shown that the formation of an adduct did not preclude FLP reactivity as long as the adduct was soluble and the FLP was accessible by an equilibrium.8 Perhaps most notably of the substrates examined activated by FLPs to date is dihydrogen as the activation of this substrate was previously thought to be the limited perview of organometallic chemistry.<sup>6,7</sup> Nonetheless, FLP chemistry has continued to broaden, with reports of activations of olefins,<sup>9-11</sup> acetylenes,<sup>11-21</sup> disulfides,  $^{22}$  CO<sub>2</sub>,  $^{23-25}$  N<sub>2</sub>O,  $^{26}$  NO<sup>27</sup> and most recently the CH bonds of propene.28

In probing the chemistry of FLPs the majority of systems examined have exploited boron-based Lewis acids although more recent studies have employed C,<sup>29–34</sup> Al,<sup>28,35–37</sup> Zr,<sup>38,39</sup> Si<sup>40</sup> and P(v)<sup>41</sup> based Lewis acids (Scheme 1). In terms of the base component, phosphorus<sup>42–57</sup> and nitrogen<sup>8,57–70</sup> based donors have dominated the FLP literature although the use of carbenes and thioethers have also been reported. In a 2010 communication, Bercaw and coworkers<sup>71</sup> described the

 $<sup>\</sup>uparrow \rm CCDC$  reference numbers 873942–873947. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30720k



Scheme 1 Examples of donor-acceptor combinations in FLP chemistry.

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combination of "Verkade's superbase" and an alkylated 9-BBN Lewis acid in FLP reactions effecting the reduction of ReCO fragments. It appeared that the poorer Lewis acidity of the 9-BBN derivative was compensated for to some extent by the "super-basicity" of  $(iPr_2N)_3PNSiMe_3$ . This finding prompted us to examine the more generalized reactivity of readily accessible, less basic phosphinimines in FLP activations of dihydrogen, carbon dioxide and phenylacetylene. Herein, we demonstrate that neither adduct formation nor the inclusion of electron withdrawing or sterically demanding substituents precludes further FLP reactivity. The implications of this extension of FLP chemistry to include phosphinimine donors is considered.

#### Experimental

#### General considerations

All preparation were done under nitrogen atmosphere in a glovebox or using standard Schlenk techniques. Solvents (hexane, pentane, toluene, diethyl ether, THF and methylene chloride) were purified with a Grubbs-type column system manufactured by Innovative Technology and stored over 4 Å molecular sieves. Deuterated solvents were dried over Na/benzophenone (C<sub>6</sub>D<sub>6</sub>, C<sub>7</sub>D<sub>8</sub>) or CaH<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>) and vacuum distilled prior to use. <sup>1</sup>H, <sup>19</sup>F, <sup>11</sup>B, <sup>31</sup>P and <sup>13</sup>C spectra were recorded at 25 °C on Varian 400 MHz and Bruker 400 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C spectra are referenced to SiMe<sub>4</sub> using the residual solvent peak impurity of the given solvent. <sup>31</sup>P, <sup>11</sup>B and <sup>19</sup>F is referenced to 85% H<sub>3</sub>PO<sub>4</sub>, BF<sub>3</sub>·OEt<sub>2</sub> and CFCl<sub>3</sub>, respectively. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values. Combustion analyses were performed inhouse employing a Perkin-Elmer CHN Analyzer.

Synthesis of Ph<sub>3</sub>PNR R = Ph (1),  $C_6F_5$  (2). Ph<sub>3</sub>PNPh and Ph<sub>3</sub>PNC<sub>6</sub>F<sub>5</sub> were prepared following modified literature methods.<sup>72</sup> To a stirred solution of Ph<sub>3</sub>PBr<sub>2</sub> (2.11 g, 5 mmol) in dry toluene (50 mL) was added  $C_6H_5NH_2$  (0.46 g, 5 mmol) and dry NEt<sub>3</sub> (7 mL) at room temperature. The mixture was then refluxed under nitrogen for 4 h, the resulting suspension was filtrated and the filtrate was evaporated to dryness. The crude product was washed with hexane, and dried under vacuum.

(1): White powder, Yield: 1.32 g (75%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.81–7.76 (m, 6H, Ph-*H*), 7.25 (d, <sup>3</sup> $J_{H-H}$  = 7 Hz, 2H, Ph-*H*), 7.19 (t, <sup>3</sup> $J_{H-H}$  = 7 Hz, 2H, Ph-*H*), 7.04–6.95 (m, 9H, Ph-*H*), 6.82 (t, <sup>3</sup> $J_{H-H}$  = 7 Hz, 1H, Ph-*H*). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): -1.3. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) partial: 152.0, 132.8 (d,  $J_{C-P}$  = 10 Hz), 131.7, 131.4, 129.1, 128.5 (d,  $J_{C-P}$  = 12 Hz), 124.0, 123.8, 117.7.

(2): White powder, Yield: 1.55 g (70%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.74–7.69 (m, 6H, Ph-*H*), 7.04–6.94 (m, 9H, Ph-*H*). <sup>19</sup>F NMR (282 Hz, C<sub>6</sub>D<sub>6</sub>): -154.7 (m, 2F, o-C<sub>6</sub>F<sub>5</sub>), -168.3 (t, <sup>3</sup>J<sub>F-F</sub> = 21 Hz, 2F, *m*-C<sub>6</sub>F<sub>5</sub>), -175.5 (m, 1F, *p*-C<sub>6</sub>F<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): 7.0. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) partial: 143.3 (dm, <sup>1</sup>J<sub>C-F</sub> = 240 Hz, *o*-C<sub>6</sub>F<sub>5</sub>), 138.7 (dm, <sup>1</sup>J<sub>C-F</sub> = 240 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 132.5 (d, J<sub>C-P</sub> = 10 Hz), 132.2, 131.8, 131.2, 128.6 (d, J<sub>C-P</sub> = 12 Hz).

Synthesis of Ph<sub>3</sub>PNtBu (3). To a stirred solution of Ph<sub>3</sub>PBr<sub>2</sub> (2.11 g, 5 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added tBuNH<sub>2</sub> (0.36 g, 5 mmol) and dry NEt<sub>3</sub> (7 mL) at room temperature. After 2 hours, cold water was added, the organic layer was dried over MgSO4 and the solvent was removed under vacuum. The crude product of [Ph<sub>3</sub>PNHtBu][Br] was washed with hexane and dried in vacuum. K[N(SiMe<sub>3</sub>)<sub>2</sub>] (0.2 g, 1 mmol) in THF solution was slowly added to a THF solution of [Ph<sub>3</sub>PNH*t*Bu][Br] (0.42 g, 1 mmol) at room temperature. The solution was allowed to stir overnight and the solvent then removed in vacuo. The residue was extracted with pentane, compound 3 was obtained as a white solid. Yield: 0.17 g (51%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.89-7.84 (m, 6H, Ph-H), 7.06–7.04 (m, 9H, Ph-H), 1.36 (s, 9H,  $CH_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz,  $C_6D_6$ ): -14.7. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $C_6D_6$ ): 136.5 (d,  $J_{C-P}$  = 96 Hz), 132.8 (d,  $J_{C-P}$  = 10 Hz), 130.3 (d,  $J_{C-P}$  = 3 Hz), 128.0 (d,  $J_{C-P}$  = 12 Hz), 51.9, 35.9 (d,  $J_{C-P}$  = 10 Hz).

Synthesis of  $Ph_3PN(Ph)B(C_6F_5)_3$  (4). To a solution of 1 (0.07 g, 0.2 mmol) dissolved in toluene (5 mL) was added  $B(C_6F_5)_3$  (0.10 g, 0.2 mmol). The reaction mixture was allowed to stir for 30 min and the volatiles were removed in vacuum. Pentane was added and the mixture filtrated and washed with pentane to give the orange solid. Yield: 0.16 g (94%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.38–7.33 (m, 6H, Ph-*H*), 7.27 (d,  ${}^{3}J_{H-H}$  = 7 Hz, 2H, Ph-*H*), 6.92 (t,  ${}^{3}J_{H-H}$  = 7 Hz, 2H, Ph-*H*), 6.74 (m, 9H, Ph-H), 6.66 (br, 1H, Ph-H). <sup>19</sup>F NMR (376 Hz, C<sub>6</sub>D<sub>6</sub>): -127.1 (s, 6F, o-C<sub>6</sub>F<sub>5</sub>), -159.5 (s, 3F, p-C<sub>6</sub>F<sub>5</sub>), -166.2 (s, 6F, m-C<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B  ${}^{1}H$  NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>): -4.0.  ${}^{31}P{}^{1}H$  NMR (162 MHz,  $C_6D_6$ : 37.2. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $C_6D_6$ ) partial: 148.7 (dm,  ${}^{1}J_{C-F} = 240$  Hz,  $o-C_{6}F_{5}$ ), 137.1 (dm,  ${}^{1}J_{C-F} = 250$  Hz,  $p-C_{6}F_{5}$ ), 137.8, 133.9 (dm,  ${}^{1}J_{C-F}$  = 250 Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 133.5 (d,  $J_{C-P}$  = 12 Hz), 130.3 (d,  $J_{C-P}$  = 15 Hz), 130.0 (d,  $J_{C-P}$  = 12 Hz), 129.1, 128.4, 128.3, 126.9, 125.6. Anal. Calcd for C42H20BF15NP: C, 58.29; H, 2.33; N, 1.62. Found: C, 58.01; H, 2.73; N, 1.53.

Synthesis of [Ph<sub>3</sub>PN(H)Ph][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (5). To a solution of 1 (0.07 g, 0.2 mmol) dissolved in toluene (5 mL) was added  $B(C_6F_5)_3$  (0.10 g, 0.2 mmol). The solution was freeze-pump thawed for three cycles and backfilled with  $H_2$  (4 atm). The solution was allowed to stir overnight at 80 °C and the volatiles were removed in vacuo. Pentane was added and the mixture filtrated and washed with pentane to give the white solid. Yield: 0.15 g (88%). Crystals for X-ray diffraction were grown from the benzene-hexane layer. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.90 (m, 2H, Ph-H), 7.80-7.71 (m, 12H, Ph-H), 7.29-7.15 (m, 4H, Ph-H), 6.87 (d,  ${}^{3}J_{H-H}$  = 8 Hz, 2H, Ph-H), 5.93 (br, 1H, N-H), 3.60 (br, 1H, B-*H*). <sup>19</sup>F NMR (376 Hz,  $CD_2Cl_2$ ): -133.7 (d,  ${}^{3}J_{F-F}$  = 22 Hz, 6F, o-C<sub>6</sub>F<sub>5</sub>), -164.2 (t,  ${}^{3}J_{F-F} = 20$  Hz, 3F, p-C<sub>6</sub>F<sub>5</sub>), -167.2 (t,  ${}^{3}J_{F-F} = 20$  Hz, 2F, p-C<sub>6</sub>F<sub>5</sub>), -167.2 (t,  ${}^{3}J_{F-F} = 20$ 20 Hz, 6F, m-C<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -23.8.  ${}^{31}P{}^{1}H$  NMR (162 MHz,  $CD_2Cl_2$ ): 34.4.  ${}^{13}C{}^{1}H$  NMR (100 MHz,  $CD_2Cl_2$ ) partial: 148.6 (dm,  ${}^{1}J_{C-F} = 240$  Hz,  $o-C_6F_5$ ), 137.9 (dm,  ${}^{1}J_{C-F}$  = 250 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 136.7 (dm,  ${}^{1}J_{C-F}$  = 250 Hz, m-C<sub>6</sub>F<sub>5</sub>), 136.4 (d,  $J_{C-P}$  = 3 Hz), 133.9 (d,  $J_{C-P}$  = 10 Hz), 130.8 (d,  $J_{C-P}$  = 15 Hz), 130.2, 129.4, 128.6, 125.9, 122.0 (d,  $J_{C-P}$  = 6 Hz), 119.6 (d,  $J_{C-P}$  = 102 Hz). Anal. Calcd for C42H22BF15NP: C, 58.16; H, 2.56; N, 1.61. Found: C, 58.73; H, 2.79; N, 1.53.

Synthesis of  $[Ph_3PN(H)R][HB(C_6F_5)_3]$  R =  $C_6F_5$  (6), *tBu* (7). These two compounds were prepared in a similar fashion and thus only one preparation is detailed. To a solution of 2 (0.089 g, 0.2 mmol) dissolved in toluene (5 mL) was added  $B(C_6F_5)_3$  (0.10 g, 0.2 mmol). The solution was freeze-pump thawed for three cycles and backfilled with H<sub>2</sub> (4 atm). The solution was allowed to stir overnight at room temperature and the volatiles were removed *in vacuo*. Pentane was added and the mixture filtrated and washed with pentane to give the white solid.

(6) Yield: 0.14 g (74%). Crystals for X-ray diffraction were grown from the benzene-hexane layer. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ : 7.92 (t,  ${}^{3}J_{H-H}$  = 7 Hz, 3H, Ph-H), 7.80–7.70 (m, 12H, Ph-H), 6.42 (br, 1H, N-H), 3.52 (br, 1H, B-H). <sup>19</sup>F NMR (376 Hz,  $CD_2Cl_2$ : -135.0 (d,  ${}^{3}J_{F-F}$  = 22 Hz, 6F, o-C<sub>6</sub>F<sub>5</sub>), -144.7 (d,  ${}^{3}J_{F-F}$  = 20 Hz, 2F, o-C<sub>6</sub>F<sub>5</sub>), -153.6 (t,  ${}^{3}J_{F-F}$  = 22 Hz, 1F, p-C<sub>6</sub>F<sub>5</sub>), -162.0 (t,  ${}^{3}J_{F-F} = 20$  Hz, 2F, m-C<sub>6</sub>F<sub>5</sub>), -165.1 (t,  ${}^{3}J_{F-F} = 22$  Hz, 3F,  $p-C_6F_5$ ), -168.2 (t,  ${}^{3}J_{F-F} = 22$  Hz, 6F,  $m-C_6F_5$ ).  ${}^{11}B{}^{1}H{}$  NMR (128 MHz,  $CD_2Cl_2$ ): -24.1. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz,  $CD_2Cl_2$ ): 42.1.  ${}^{13}C{}^{1}H$  NMR (100 MHz,  $CD_2Cl_2$ ) partial: 148.0 (dm,  ${}^{1}J_{C-F}$ = 250 Hz, o-C<sub>6</sub>F<sub>5</sub>), 144.7 (dm,  ${}^{1}J_{C-F}$  = 244 Hz, o-C<sub>6</sub>F<sub>5</sub>), 141.2 (dm,  ${}^{1}J_{C-F} = 245$  Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 137.5 (dm,  ${}^{1}J_{C-F} = 244$  Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 136.3 (dm,  ${}^{1}J_{C-F}$  = 250 Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 136.4 (d,  $J_{C-P}$  = 3 Hz), 133.6 (d,  $J_{C-P}$  = 12 Hz), 130.3 (d,  $J_{C-P}$  = 14 Hz), 124.3, 119.3 (d,  $J_{C-P}$  = 102 Hz), 110.5. Anal. Calcd for C42H17BF20NP: C, 52.69; H, 1.79; N, 1.46. Found: C, 52.44; H, 2.06; N, 1.52.

(7) Yield: 0.12 g (72%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.90–7.72 (m, 15H, Ph-*H*), 3.63 (br, 1H, B-*H*), 3.35 (br, 1H, N-*H*), 1.30 (s, 9H, CH<sub>3</sub>). <sup>19</sup>F NMR (376 Hz, CD<sub>2</sub>Cl<sub>2</sub>): -134.9 (d,  ${}^{3}J_{F-F} = 22$  Hz, 6F, o-C<sub>6</sub>F<sub>5</sub>), -165.2 (t,  ${}^{3}J_{F-F} = 22$  Hz, 3F, p-C<sub>6</sub>F<sub>5</sub>), -168.4 (t,  ${}^{3}J_{F-F} = 22$  Hz, 6F, m-C<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -24.9. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 33.4. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) partial: 148.2 (dm,  ${}^{1}J_{C-F} = 248$  Hz, o-C<sub>6</sub>F<sub>5</sub>), 137.4 (dm,  ${}^{1}J_{C-F} = 244$  Hz, p-C<sub>6</sub>F<sub>5</sub>), 136.3 (dm,  ${}^{1}J_{C-F} = 250$  Hz, m-C<sub>6</sub>F<sub>5</sub>), 135.5, 133.4 (d,  $J_{C-P} = 12$  Hz), 130.3 (d,  $J_{C-P} = 14$  Hz), 121.2 (d,  $J_{C-P} = 102$  Hz), 124.2, 56.5, 31.3. Anal. Calcd for C<sub>40</sub>H<sub>26</sub>BF<sub>15</sub>NP: C, 56.69; H, 3.09; N, 1.65. Found: C, 56.92; H, 3.13; N, 1.64.

**Ph**<sub>3</sub>**PN**(**R**)**COOB**(**C**<sub>6</sub>**F**<sub>5</sub>)<sub>3</sub> **R** = **Ph** (8), **C**<sub>6</sub>**F**<sub>5</sub> (9). These two compounds were prepared in a similar fashion and thus only one preparation is detailed. To a solution of **1** (0.089 g, 0.2 mmol) dissolved in toluene (5 mL) was added  $B(C_6F_5)_3$  (0.10 g, 0.2 mmol). The solution was freeze-pump thawed for three cycles and backfilled with CO<sub>2</sub> (1 atm). The solution was allowed to stir 1 h at room temperature and the volatiles were removed *in vacuo*. Pentane was added and the mixture filtrated and washed with pentane to give the white solid.

(8) Yield: 0.15 g (83%). Crystals for X-ray diffraction were grown from the benzene–hexane layer. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.79–7.75 (m, 3H, Ph-*H*), 7.66–7.57 (m, 12H, Ph-*H*), 7.23–7.18 (m, 3H, Ph-*H*), 7.14–7.11 (m, 2H, Ph-*H*). <sup>19</sup>F NMR (376 Hz, CD<sub>2</sub>Cl<sub>2</sub>): -136.4 (d,  ${}^{3}J_{F-F} = 20$  Hz, 6F, o-C<sub>6</sub>F<sub>5</sub>), -162.6 (t,  ${}^{3}J_{F-F} = 20$  Hz, 3F, p-C<sub>6</sub>F<sub>5</sub>), -167.8 (td,  ${}^{3}J_{F-F} = 20$  Hz,  ${}^{5}J_{F-F} = 9$  Hz, 6F, m-C<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -3.6. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 41.9. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) partial: 148.2 (dm,  ${}^{1}J_{C-F} = 240$  Hz, o-C<sub>6</sub>F<sub>5</sub>),

136.6 (dm,  ${}^{1}J_{C-F}$  = 250 Hz, m-C<sub>6</sub>F<sub>5</sub>), 135.2 (d,  $J_{C-P}$  = 3 Hz), 134.1 (d,  $J_{C-P}$  = 12 Hz), 130.6 (d,  $J_{C-P}$  = 15 Hz), 130.0, 129.5, 129.1, 120.9, 119.9. Anal. Calcd for C<sub>43</sub>H<sub>20</sub>BF<sub>15</sub>NO<sub>2</sub>P: C, 56.79; H, 2.22; N, 1.54. Found: C, 57.12; H, 2.22; N, 1.74.

(9) Yield: 0.16 g (80%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.85–7.35 (m, 15H, Ph-*H*). <sup>19</sup>F NMR (376 Hz, CD<sub>2</sub>Cl<sub>2</sub>): –135.9 (d, <sup>3</sup> $J_{F-F}$  = 22 Hz, 6F, o-C<sub>6</sub>F<sub>5</sub>), –142.5 (d, <sup>3</sup> $J_{F-F}$  = 20 Hz, 2F, o-C<sub>6</sub>F<sub>5</sub>), –150.6 (t, <sup>3</sup> $J_{F-F}$  = 22 Hz, 1F, p-C<sub>6</sub>F<sub>5</sub>), –160.7 (t, <sup>3</sup> $J_{F-F}$  = 22 Hz, 3F, p-C<sub>6</sub>F<sub>5</sub>), –161.8 (t, <sup>3</sup> $J_{F-F}$  = 20 Hz, 2F, m-C<sub>6</sub>F<sub>5</sub>), –166.4 (t, <sup>3</sup> $J_{F-F}$  = 22 Hz, 6F, m-C<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>): –2.8. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 44.7. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) partial: 148.0 (dm, <sup>1</sup> $J_{C-F}$  = 250 Hz, o-C<sub>6</sub>F<sub>5</sub>), 144.7 (dm, <sup>1</sup> $J_{C-F}$  = 244 Hz, o-C<sub>6</sub>F<sub>5</sub>), 141.2 (dm, <sup>1</sup> $J_{C-F}$  = 245 Hz, p-C<sub>6</sub>F<sub>5</sub>), 137.5 (dm, <sup>1</sup> $J_{C-F}$  = 244 Hz, p-C<sub>6</sub>F<sub>5</sub>), 136.3 (dm, <sup>1</sup> $J_{C-F}$  = 250 Hz, m-C<sub>6</sub>F<sub>5</sub>), 134.8, 134.4 (d, *J* = 3 Hz), 133.4 (d, *J* = 10 Hz), 130.3 (d, *J* = 14 Hz), 129.9 (d, *J* = 14 Hz), 129.3 (d, *J* = 14 Hz), 128.5, 125.5 (d, *J* = 109 Hz). Anal. Calcd for C<sub>43</sub>H<sub>15</sub>BF<sub>20</sub>NO<sub>2</sub>P: C, 51.68; H, 1.51; N, 1.40. Found: C, 51.94; H, 1.76; N, 1.54.

 $[Ph_3PN(H)R][PhC \equiv CB(C_6F_5)_3]$  R = Ph (10), *tBu* (12). All these compounds were prepared in a similar fashion and thus only one preparation is detailed. To a solution of 1 (0.035 g, 0.2 mmol) dissolved in toluene (5 mL) was added  $B(C_6F_5)_3$  (0.051 g, 0.2 mmol) and PhC =CH (0.01 g, 0.1 mmol). The solution was allowed to stir for 2 h at room temperature and the filtrated. The residue was washed with pentane and dried under vacuum.

(10) Yield: 0.08 g (82%). Crystals for X-ray diffraction were grown from the toluene-hexane layer. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.92-7.89 (m, Ph-H), 7.76-7.68 (m, Ph-H), 7.60-7.50 (m, Ph-H), 7.27-7.15 (m, Ph-H), 6.91-6.87 (m, Ph-H), 5.68 (br, N-H). <sup>19</sup>F NMR (376 Hz,  $CD_2Cl_2$ ): -132.8 (d,  ${}^{3}J_{F-F}$  = 20 Hz, 6F,  $o-C_6F_5$ , **10b**), -133.1 (d,  ${}^{3}J_{F-F}$  = 20 Hz, 6F,  $o-C_6F_5$ , **10b**), -133.7 (d,  ${}^{3}J_{F-F} = 22$  Hz, 6F, o-C<sub>6</sub>F<sub>5</sub>, **10a**), -164.8 (t,  ${}^{3}J_{F-F} = 20$  Hz, 3F,  $p-C_6F_5$ , **10a**), -165.0 (t,  ${}^{3}J_{F-F} = 20$  Hz, 3F,  $p-C_6F_5$ , **10b**), -165.4 (t,  ${}^{3}J_{F-F} = 20$  Hz, 3F, *p*-C<sub>6</sub>F<sub>5</sub>, **10b**), -168.2 (t,  ${}^{3}J_{F-F} = 20$  Hz, 6F, m-C<sub>6</sub>F<sub>5</sub>, **10a**), -168.8 (t,  ${}^{3}J_{F-F}$  = 20 Hz, 6F, m-C<sub>6</sub>F<sub>5</sub>, **10b**), -168.9 (t,  ${}^{3}J_{F-F} = 20$  Hz, 6F, *m*-C<sub>6</sub>F<sub>5</sub>, **10b**).  ${}^{11}B{}^{1}H{}$  NMR (128 MHz,  $CD_2Cl_2$ : -16.5 (br), -20.9 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): 38.4(10b), 34.6 (10a). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) partial: 148.5 (dm,  ${}^{1}J_{C-F}$  = 240 Hz, o-C<sub>6</sub>F<sub>5</sub>), 137.2 (dm,  ${}^{1}J_{C-F}$  = 250 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 136.3 (dm,  ${}^{1}J_{C-F}$  = 250 Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 136.5 (d,  $J_{C-P}$  = 3 Hz), 134.9, 133.8 (d,  $J_{C-P}$  = 12 Hz), 131.5, 130.9 (d,  $J_{C-P}$  = 15 Hz), 129.9, 129.7, 128.4, 126.0, 121.5 (d,  $J_{C-P} = 6$  Hz), 119.3 (d,  $J_{C-P}$  = 102 Hz). Anal. Calcd for C<sub>50</sub>H<sub>26</sub>BF<sub>15</sub>NP: C, 62.07; H, 2.71; N, 1.45. Found: C, 62.53; H, 2.76; N, 1.53.

(12) Yield: 0.085 g (89%). Crystals for X-ray diffraction were grown from the toluene–hexane layer. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.90–7.86 (m, 3H, Ph-*H*), 7.83–7.72 (m, 12H, Ph-*H*), 7.34–7.31 (m, 2H, Ph-*H*), 7.22–7.12 (m, 3H, Ph-*H*), 3.22 (d,  ${}^{3}J_{P-H} = 8$  Hz, N-*H*), 1.28 (s, 9H, CH<sub>3</sub>). <sup>19</sup>F NMR (376 Hz, CD<sub>2</sub>Cl<sub>2</sub>): –133.6 (d,  ${}^{3}J_{F-F} = 22$  Hz, 6F, o-C<sub>6</sub>F<sub>5</sub>), –164.8 (t,  ${}^{3}J_{F-F} = 22$  Hz, 3F, p-C<sub>6</sub>F<sub>5</sub>), –168.3 (t,  ${}^{3}J_{F-F} = 20$  Hz, 6F, m-C<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>): –20.9. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 33.4. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) partial: 148.4 (dm, <sup>1</sup>J<sub>C-F</sub> = 244 Hz, o-C<sub>6</sub>F<sub>5</sub>), 138.7 (dm, <sup>1</sup>J<sub>C-F</sub> = 242 Hz, p-C<sub>6</sub>F<sub>5</sub>), 136.7 (dm, <sup>1</sup>J<sub>C-F</sub> = 242 Hz, m-C<sub>6</sub>F<sub>5</sub>), 136.0, 133.6 (d,  $J_{C-P} =$ 

10 Hz), 131.5, 130.7 (d,  $J_{C-P}$  = 14 Hz), 128.2, 126.1, 121.5 (d,  $J_{C-P}$  = 102 Hz), 56.9, 32.0. Anal. Calcd for C<sub>48</sub>H<sub>30</sub>BF<sub>15</sub>NP: C, 60.84; H, 3.19; N, 1.48. Found: C, 60.59; H, 3.19; N, 1.46.

 $(Ph_3PN(H)C_6F_5)(Ph)C = C(H)B(C_6F_5)_3$  (11). This species was prepared in an analogous fashion to that described for 10 and 12 above.

(11) Yield: 0.092 g (87%). Crystals for X-ray diffraction were grown from the toluene-hexane layer. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.83-7.73 (m, Ph-H), 7.70-7.56 (m, Ph-H), 7.20-7.17 (m, Ph-H), 7.13-7.07 (m, Ph-H), 6.94-6.84 (m, Ph-H), 6.64 (br, Z-C=CH), 5.50 (br, E-C=CH). <sup>19</sup>F NMR (376 Hz, CD<sub>2</sub>Cl<sub>2</sub>): -133.2 (d,  ${}^{3}J_{F-F} = 22$  Hz, 6F, Z-o-C<sub>6</sub>F<sub>5</sub>), -133.7 (d,  ${}^{3}J_{F-F} = 22$  Hz, 6F, *E-o*-C<sub>6</sub>F<sub>5</sub>), -139.2 (d,  ${}^{3}J_{F-F}$  = 20 Hz, 2F, *Z-o*-C<sub>6</sub>F<sub>5</sub>), -144.5 (d,  ${}^{3}J_{F-F} = 22$  Hz, 2F, *E-o*-C<sub>6</sub>F<sub>5</sub>), -151.8 (t,  ${}^{3}J_{F-F} = 22$  Hz, 1F, *Z-p*- $C_6F_5$ ), -152.9 (t,  ${}^{3}J_{F-F}$  = 22 Hz, 1F, *E*-*p*- $C_6F_5$ ), -161.3 (t,  ${}^{3}J_{F-F}$  = 20 Hz, 2F, *E-m*-C<sub>6</sub>F<sub>5</sub>), -163.0 (t,  ${}^{3}J_{F-F}$  = 20 Hz, 2F, *Z-m*-C<sub>6</sub>F<sub>5</sub>), -164.6 (t,  ${}^{3}J_{F-F} = 22$  Hz, 3F, *E-p*-C<sub>6</sub>F<sub>5</sub>), -164.9 (t,  ${}^{3}J_{F-F} = 22$  Hz, 3F, Z-p-C<sub>6</sub>F<sub>5</sub>), -166.7 (t,  ${}^{3}J_{F-F}$  = 22 Hz, 6F, Z-m-C<sub>6</sub>F<sub>5</sub>), -168.2 (t,  ${}^{3}J_{F-F} = 20$  Hz, 6F, *E-m*-C<sub>6</sub>F<sub>5</sub>).  ${}^{11}B{}^{1}H{}$  NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -16.7 (Z), -20.9 (E). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 42.3 (E), 41.8 (Z). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) partial: 148.4 (dm,  ${}^{1}J_{C-F} = 240 \text{ Hz}, o-C_{6}F_{5}$ , 137.0, 135.7, 134.9 (d,  $J_{C-P} = 10 \text{ Hz}$ ), 134.0 (d,  $J_{C-P}$  = 12 Hz), 131.5, 130.8 (d,  $J_{C-P}$  = 14 Hz), 130.1 (d,  $J_{C-P}$  = 14 Hz), 129.4, 128.8, 128.5, 128.3, 127.7, 126.3, 125.5, 119.8 (d, J<sub>C-P</sub> = 100 Hz), 118.3 (d,  $J_{C-P}$  = 14 Hz). Anal. Calcd for  $C_{50}H_{21}BF_{20}NP$ : C, 56.79; H, 2.00; N, 1.32. Found: C, 57.24; H, 2.05; N, 1.31.

#### X-ray data collection, reduction, solution and refinement

Table 1 Crystallographic data

Single crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an  $N_2$ stream. The data were collected on a Bruker Apex II diffractometer (see Table 1). The data were collected at  $150(\pm 2)$  or  $293(\pm 2)$  K for all crystals. Data reduction was performed using the SAINT software package and an absorption correction applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on  $F^2$  using XL as implemented in the SHELXTL suite of programs.<sup>73</sup> All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors (see ESI<sup>†</sup>).

## **Results and discussion**

The phosphinimines  $Ph_3PNR$  (R = Ph 1, C<sub>6</sub>F<sub>5</sub> 2) were prepared by a modified literature preparation via reactions of Ph<sub>3</sub>PBr<sub>2</sub> and the corresponding arylamine. The related species Ph<sub>3</sub>PNtBu 3 was prepared in an analogous manner although the intermediate product [Ph3PNHtBu][Br] required use of  $K[N(SiMe_3)_2]$  to afford 3. To probe the potential of these phosphinimines in FLP reactions, these species were first reacted with  $B(C_6F_5)_3$ . In the case of 1 combination with  $B(C_6F_5)_3$ resulted in the formation of an orange solid which was isolated in 94% yield. This product 4 exhibits a <sup>11</sup>B{<sup>1</sup>H} NMR resonance at -4.0 ppm and <sup>19</sup>F NMR signals at -127.1, -159.5 and -166.2 ppm. These data are consistent with the presence of four coordinated boron. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a peak at 37.2 ppm significantly downfield from the precursor phosphinimine. These together with the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data are consistent with the formulation of 4 as the phosphinimine-borane adduct Ph<sub>3</sub>PN(Ph)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. In contrast, compounds 2 and 3 in combination with  $B(C_6F_5)_3$  show no apparent reaction. The resulting mixtures are best described as FLPs and presumably result from the diminished donor ability of 2 and the increased steric demands of 3.

#### Reactions with hydrogen

Despite the ability of 1 to react with  $B(C_6F_5)_3$ , the addition of dihydrogen to a solution of 4 and stirring of the mixture at

5	6	8	10	11	12
C48H28BF15NP	C42H17BF20NP	$\mathrm{C}_{49}\mathrm{H}_{26}\mathrm{BF}_{15}\mathrm{NO}_{2}\mathrm{P}$	C <sub>50</sub> H <sub>26</sub> BF <sub>15</sub> NP	C55.25H27BF20NP	C48H30BF15NP
945.49	957.35	987.49	967.50	1126.56	947.51
Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
10.1234(5)	11.7826(7)	9.1433(8)	10.7176(5)	23.6597(5)	10.1999(8)
11.7781(6)	16.5070(10)	17.7446(16)	24.4998(11)	19.1776(4)	17.1867(13)
17.6664(9)	19.9076(13)	26.879(3)	15.8572(7)	24.7362(5)	24.1364(19)
82.839(2)	90.00	90.00	90.00	90.00	89.968(4)
83.646(2)	94.530(2)	92.266(3)	97.100(2)	117.8180(10)	80.171(4)
83.741(2)	90.00	90.00	90.00	90.00	83.358(4)
2067.47(18)	3859.8(4)	4357.6(7)	4131.8(3)	9926.6(4)	4140.3(6)
2	4	4	4	8	4
1.519	1.647	1.505	1.555	1.508	1.520
0.172	0.203	0.170	0.174	0.171	0.172
32 322	34 172	37 373	68 246	83 412	69 928
7265	8872	9946	9497	22 636	18 865
5733	5638	7243	6714	13 976	13 852
594	594	622	613	1402	1197
0.0410	0.0514	0.0576	0.0401	0.0587	0.0403
0.1108	0.1336	0.1616	0.1127	0.1980	0.1082
1.025	0.997	1.046	0.873	1.058	1.037
	$\frac{5}{5}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$



Scheme 2 Synthesis of 5–7.



Fig. 1 POV-ray depiction of 5. Of the hydrogen atoms, only the BH and NH protons are shown. C: black; F: pink; B: green; P: orange; N: blue; H: turquoise.

80 °C overnight resulted in the formation of a new product 5. This species was precipitated by addition of pentane as a white solid in 88% yield. The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum showed a resonance at -23.8 ppm while the <sup>19</sup>F NMR spectrum showed peaks at -133.7, -164.2 and -167.2 ppm, consistent with the generation of the hydridoborate anion HB( $C_6F_5$ )<sub>3</sub>. The <sup>31</sup>P{<sup>1</sup>H} NMR data showed a slightly shifted signal at 34.4 ppm. Resonances at 5.93 and 3.60 ppm in the <sup>1</sup>H NMR spectrum were attributed to NH and BH fragments. These data infer that 5 is  $[Ph_3PN(H)Ph][HB(C_6F_5)_3]$  (Scheme 2). This was subsequently confirmed following the isolation of crystals for X-ray diffraction from the toluene-hexane (Fig. 1). The P-N distance was 1.641(2) Å. The remaining metric parameters are unexceptional. The formation of 5 establishes that there is a small equilibrium governing the formation of 4. A similar situation in which an adduct exhibited FLP reactivity has been described for the combination of lutidine and  $B(C_6F_5)_3$ .<sup>8,65</sup>

In a similar fashion, the phosphinimines 2 and 3 were combined with  $B(C_6F_5)_3$  and stirred overnight under 4 atm of  $H_2$  at 25 °C. These reactions resulted in the formation of the white salts  $[Ph_3PN(H)R][HB(C_6F_5)_3] R = C_6F_5 6$  and *t*Bu 7, respectively (Scheme 2). These products were isolated in 74 and 72% yields and the spectroscopic data of 6 and 7 were similar to those described for 5. In the case of 6, the formulation was further confirmed by X-ray diffraction studies (Fig. 2). The B–H and N–H distances were similar to those found in 5, while the P–N



Fig. 2 POV-ray depiction of 6. Of the hydrogen atoms, only the BH and NH protons are shown. C: black; F: pink; B: green; P: orange; N: blue; H: turquoise.

distance in **6** was found to be 1.645(2) Å. Again, the B–H···H–N separation was short being 2.01 Å, suggestion the presence of dihydrogen bonding in the solid state.

#### Reactions with carbon dioxide

The combinations of the phosphinimine Lewis bases 1 or 2 with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> also react with carbon dioxide at room temperature to give the white solids 8 and 9 in 83 and 80% yields respectively. Compound 8 exhibits <sup>19</sup>F NMR signals at -136.4, -162.6 and -167.8 ppm and a <sup>11</sup>B{<sup>1</sup>H} NMR resonance at -3.6 ppm. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **8** shows a resonances at 41.9 ppm. These data are very similar to those observed for 9 and infer the formulation of these products as Ph<sub>3</sub>PN(R)C(O)- $OB(C_6F_5)_3$  R = Ph 8,  $C_6F_5$  9 (Scheme 3). (8) In the case of 8 this formulation was confirmed via a crystallographic study (Fig. 3). The P-N and B-O bond lengths in 8 were found to be 1.671(2) Å and 1.526(3) Å, respectively while the terminal and bridging C-O bond distances were determined to be 1.214(3) Å and 1.288(3) Å, respectively. These C-O bond lengths are comparable to 1.2081(15)/1.2988(15) Å and 1.209(4)/1.284(4) Å observed in tBu<sub>3</sub>P(CO<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-(CO<sub>2</sub>), respectively.<sup>23</sup> The B-O distance in 8 is slightly shorter than the B-O distances of 1.5474(15) Å and 1.550(4) Å reported in these two phosphine-borane-CO2 complexes.

The isolation of 8 and 9 is interesting given that compounds 1-3 are known to react with CO<sub>2</sub> on their own to



Scheme 3 Synthesis and reactivity of 8 and 9.

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Fig. 3 POV-ray depiction of 8. No hydrogen atoms shown. C: black; F: pink; B: green; P: orange; N: blue; O: red.

generate phosphine-oxide and the isocyanate RNCO derived from the terminal imide fragment on the phosphinimine.<sup>74</sup> In contrast to 1 and 2, compound 3 together with  $B(C_6F_5)_3$  reacts with  $CO_2$  rapidly to give  $Ph_3P = OB(C_6F_5)_3$  and tBuN = C = O. No intermediate  $CO_2$  species were intercepted in this case. This may result in part from the stronger basicity of 3 compared to the other phosphinimines. Presumably, in this case, the transient  $CO_2$  species is highly reactive and as a result of this enhanced basicity, thus prompting rapid formation of phosphineoxide and isocyante. It is also noteworthy that compounds 8 and 9 are not stable, and transform to  $Ph_3P = OBC (C_6F_5)_3$  and R-N = C = O when left in solution for several days. Alternatively heating to 60 °C for 30 min affords conversion of 8 and 9 to the borane adduct of the corresponding phosphineoxide and isocyanate.

#### Reactions with phenylacetylene

Reactions of the FLPs derived from 1-3 with  $B(C_6F_5)_3$  with phenylacetylene generate new products 10-12, in 82, 87 and 89% yields, respectively. In the case of 10, two isomers of the product were observed in a 80:20 ratio as evidenced by the  ${}^{31}P{}^{1}H$  NMR resonances at 34.6 (10a) and 38.4 (10b) ppm and the sharp  ${}^{11}B{}^{1}H$  NMR signal at -20.9 ppm and the broader signal at -16.5 ppm. Similarly the <sup>19</sup>F NMR spectrum showed two sets of signals. In the case of 10a signals were observed at -133.7, -164.8 and -168.2 ppm while for 10b the resonances were seen at -132.8, -133.1, -165.0, -165.4, -168.8 and -168.9 ppm. In the <sup>1</sup>H NMR spectrum the most notable signal is observed at 5.68 ppm which is indicative of phosphinimonium salt. (br, N-H). Collectively these data infer the formation of  $[Ph_3PN(H)Ph][PhC \equiv CB(C_6F_5)_3]$  10a as the major product together with a minor amount of the addition product  $(Ph_3PNPh)(Ph)C = CH(B(C_6F_5)_3)$  10b (Scheme 4). The formulation of 10a was subsequently confirmed via a crystallographic study (Fig. 4). The metric parameters were unexceptional. The formation of both 10a and 10b, albeit in a 80:20 ratio, is a further demonstration of the two reaction pathways for the reactions of FLPs with phenylacetylene.15,16

The corresponding reaction that yielded **11** also showed the formation of two isomers **11a** and **11b** in a 3 : 1 ratio. However



Scheme 4 Synthesis of 10–12.



Fig. 4 POV-ray depiction of **10a**. Of the hydrogen atoms, only the NH proton is shown. C: black; F: pink; B: green; P: orange; N: blue; H: turquoise.



Fig. 5 POV-ray depiction of **11a**. Of the hydrogen atoms, only the CH proton is shown. C: black; F: pink; B: green; P: orange; N: blue; H: turquoise.

in contrast to **10**, the <sup>31</sup>P{<sup>1</sup>H} and <sup>11</sup>B{<sup>1</sup>H} signals were more similar for the two species giving signals at 42.3 and 41.8 ppm and -20.9 and -16.7 ppm, respectively. These isomers were attributed to the E (**11a**) and Z (**11b**) isomers of the addition products. In addition to the other NMR data, this notion was further supported by a crystallographic study (Fig. 5). The newly formed N–C bond is found to be 1.433(2) Å, while the olefinic bond is 1.387(3) Å. In the case of **11**, the reduced basicity of the phosphinimine **2** results in the exclusive formation



Fig. 6 POV-ray depiction of 12. Of the hydrogen atoms, only the NH proton is shown. C: black; F: pink; B: green; P: orange; N: blue; H: turquoise.

of the addition products. The dominant E-isomer is consistent with that observed for phosphine–borane additions to alkynes. Interestingly no evidence was previous reported for formation of the Z-addition products for related termolecular reactions. Indeed, it is only in chelated FLP systems where *cis*-addition products have been previously observed.<sup>12,37</sup>

The last of these reactions with phenylacetylene afforded the product **12**. In this case only a single product was observed as it gave rise to a single <sup>31</sup>P{<sup>1</sup>H} resonance at 33.4 ppm and a <sup>11</sup>B{<sup>1</sup>H} signal at -20.9 ppm. The <sup>1</sup>H NMR spectral data, in particular the phosphorus coupled doublet at 3.22 ( ${}^{3}J_{P-H} = 8$  Hz) inferred the formation of a phosphinimonium salt and thus the formulation of **12** as [Ph<sub>3</sub>PN(H)*t*BuR][PhC=CB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]. This was verified by a crystal structure of **12** (Fig. 6). It seems clear that the increased basicity of **3** results in the exclusive formation of the deprotonation product, the phosphinimonium salt **12**.

## Conclusions

The reactions described herein demonstrated that phosphinimines are effective base partners for FLP reactions. Even in the case of **1** where a classical Lewis-acid–base adduct is isolable, the combination of these phosphinimines of the form  $Ph_3PNR$  with  $B(C_6F_5)_3$  are capable of effecting the activation of  $H_2$ ,  $CO_2$  and phenylacetylene. These findings serve to broaden the range of acid–base combinations for FLP reactivity. We are continuing probe new combinations of Lewis acids and bases in the quest for more reactive FLP systems for the activation of small molecules and applications in catalysis.

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