

## Supporting Information

### Access to adducts of parent iminoborane isomers, HBNH and NBH<sub>2</sub>, using frustrated Lewis pair chelation

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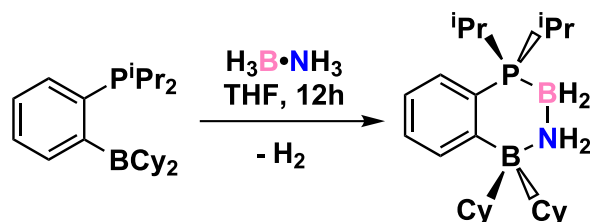
#### 1. General information, materials and instrumentation

Unless specified, all reactions were performed under an inert atmosphere of N<sub>2</sub> using standard Schlenk or glovebox (Innovative Technology, Inc. or MBraun) techniques. All solvents (except heptane, hexamethyldisiloxane, and pentane) were dried using a solvent purification system (manufactured by Innovative Technology, Inc.) and stored over 4 Å molecular sieves under a nitrogen atmosphere prior to use. Heptane was sparged with N<sub>2</sub> for 30 minutes prior to use. Pentane was degassed via three freeze-pump-thaw cycles, and dried over 4 Å molecular sieves prior to use. Hexamethyldisiloxane was refluxed over calcium hydride overnight under an N<sub>2</sub> atmosphere, distilled, and stored over 4 Å molecular sieves. Potassium bis(trimethylsilyl)amide (K[N(SiMe<sub>3</sub>)<sub>2</sub>]) was purchased from Sigma-Aldrich and recrystallized from a saturated toluene solution at -40 °C prior to use. Dimethylsulfide (Me<sub>2</sub>S) and trimethylsilyl azide (Me<sub>3</sub>SiN<sub>3</sub>) were purchased from Sigma-Aldrich and stored over 4 Å molecular sieves at -40 °C under N<sub>2</sub>. All other chemicals were purchased from Sigma-Aldrich and used as received. **PB**<sup>S1</sup> was synthesized according to a literature procedure. Bi<sub>3</sub><sup>S2</sup> and Me<sub>2</sub>S•Bi<sub>3</sub><sup>S3</sup> were synthesized according to modified synthetic procedures with further details presented below.

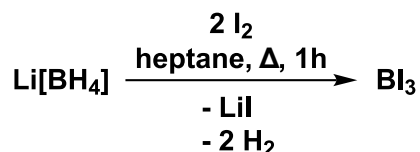
<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P and <sup>11</sup>B NMR spectra were recorded at room temperature using an Agilent/Varian Inova-400, DD2 MR-400, VNMRS-500, or VNMRS-700 spectrometer and referenced to Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}), Me<sub>4</sub>Si-*d*<sub>12</sub> (<sup>2</sup>H), 85 % H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P), 15 % F<sub>3</sub>B•OEt<sub>2</sub> (<sup>11</sup>B), and 9.7 M LiCl in D<sub>2</sub>O (<sup>7</sup>Li). Chemical shifts are reported in parts per million (ppm) and coupling constants

(*J*) are reported in Hertz (Hz). Elemental analyses (EA) were performed at the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp apparatus and are uncorrected. Infrared (IR) spectra were recorded either as dropcast films from CH<sub>2</sub>Cl<sub>2</sub> solutions, powders, or Nujol mulls on KBr plates with a Nicolet IR100 FTIR spectrometer. Single crystal X-ray crystallography was performed using a Bruker D8 Duo or PLATFORM diffractometer, equipped with a SMART APEX II CCD area detector.

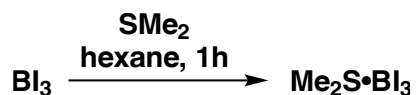
## 2. Experimental procedures



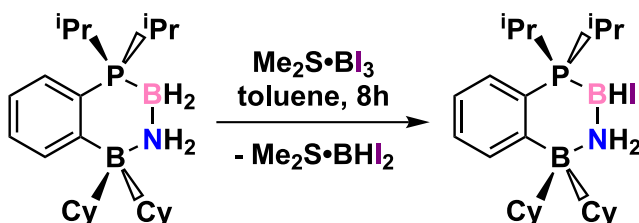
**Synthesis of PB{H<sub>2</sub>BNH<sub>2</sub>}**: A solution of H<sub>3</sub>N•BH<sub>3</sub> (0.0117 g, 0.379 mmol) in 5 mL of THF was added to a solution of <sup>i</sup>Pr<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub> (**PB**<sup>S1</sup>) (0.138 g, 0.373 mmol) in 5 mL of THF. After stirring the mixture for 12 hours at room temperature, the volatiles were removed under vacuum. To the crude reaction mixture was then added 5 mL of hexanes, then the mixture was filtered through Celite and the volatiles were removed from the filtrate to give **PB{H<sub>2</sub>BNH<sub>2</sub>}** as a white solid (0.1125 g, 75 %). Colorless X-ray quality crystals of **PB{H<sub>2</sub>BNH<sub>2</sub>}** were grown out of a concentrated solution of cold (-40 °C) hexanes. <sup>1</sup>H{<sup>11</sup>B} NMR (498.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.77 (dd, <sup>3</sup>J<sub>HP</sub> = 3.6 Hz, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 1H, ArCH), 7.26 – 7.28 (m, 1H, ArCH), 6.95 – 6.97 (m, 1H, ArCH), 6.88 – 6.91 (m, 1H, ArCH), 2.42 (br d, <sup>1</sup>J<sub>BH</sub> = ca. 138 Hz, 2H, BH<sub>2</sub>), 2.00 (br d, <sup>2</sup>J<sub>HH</sub> = 12.6 Hz, 2H, CyCH<sub>2</sub>), 1.87 – 1.95 (m, 6H, CyCH<sub>2</sub>), 1.76 – 1.82 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.64 – 1.72 (m, 2H, CyCH<sub>2</sub>), 1.43 – 1.61 (m, 4H, CyCH<sub>2</sub>), 1.32 – 1.37 (m, 2H, CyCH<sub>2</sub>), 1.02 – 1.08 (m, 2H, CyCH<sub>2</sub>), 0.81 – 0.92 (m, 4H, CyCH<sub>2</sub> & CyCH), 0.86 (dd, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, <sup>3</sup>J<sub>HP</sub> = 15.4 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.80 (dd, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, <sup>3</sup>J<sub>HP</sub> = 13.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the resonance for the NH<sub>2</sub> protons could not be located.* <sup>13</sup>C{<sup>1</sup>H} NMR (176.0 MHz, C<sub>6</sub>D<sub>6</sub>): δ 135.1 (d, *J*<sub>CP</sub> = 14.1 Hz, ArCH), 130.5 (d, *J*<sub>CP</sub> = 3.7 Hz, ArCH), 130.0 (d, *J*<sub>CP</sub> = 2.6 Hz, ArCH), 123.6 (d, *J*<sub>CP</sub> = 7.9 Hz, ArCH), 120.9 (d, <sup>1</sup>*J*<sub>CP</sub> = 50.5 Hz, ArC), 34.6 (br, CyCH), 31.7 (s, CyCH<sub>2</sub>), 30.9 (s, CyCH<sub>2</sub>), 30.2 (s, CyCH<sub>2</sub>), 29.9 (s, CyCH<sub>2</sub>), 28.5 (s, CyCH<sub>2</sub>), 23.1 (d, <sup>1</sup>*J*<sub>CP</sub> = 36.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 17.1 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 16.9 (s, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the resonance for the ArC bound to boron could not be located.* <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 3.5 (br, <sup>i</sup>Pr<sub>2</sub>P). <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ -6.0 (br, BCy<sub>2</sub>, FWHM = 180 Hz), -24.6 (br, BH<sub>2</sub>, FWHM = 160 Hz). Selected IR bands (Nujol mull, cm<sup>-1</sup>): 2727 (s, νB-H), 3322 (s, νN-H), 3280 (s, νN-H). Anal. Calcd. for C<sub>24</sub>H<sub>44</sub>B<sub>2</sub>NP: C 72.21, H 11.11, N 3.51; Found: C 72.16, H 11.06, N 3.55. m.p. 110 – 112 °C.



**Synthesis of BI<sub>3</sub>:** This compound was made according to a modified literature procedure.<sup>52</sup> Iodine (I<sub>2</sub>, 25.0 g, 98.5 mmol) was quickly added to a stirring solution of Li[BH<sub>4</sub>] (1.07 g, 49.3 mmol) in 40 mL of heptane, resulting in a purple reaction mixture. The reaction mixture was then heated to reflux for 1 hour, leading to the full consumption of I<sub>2</sub>, which was observed by a color change from purple to yellow for the reaction mixture. After removing the volatiles under vacuum, the crude product was loaded into a sublimation apparatus and heated at 40 °C for 24 hours at 0.020 mBar to afford pure colorless crystals of BI<sub>3</sub> on the water-cooled sublimation finger. The recovered crystals (8.06 g, 42 %) were stored in the freezer at -40 °C prior to use. <sup>11</sup>B{<sup>1</sup>H} NMR (159.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ -7.5 (s, BI<sub>3</sub>).

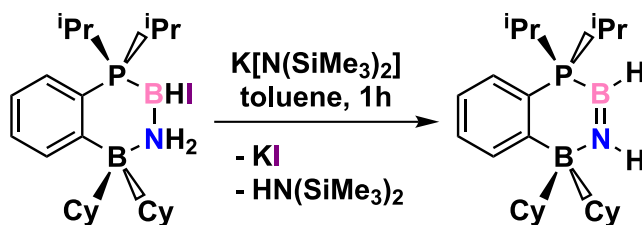


**Synthesis of Me<sub>2</sub>S•BI<sub>3</sub>:** This compound was made according to a modified literature procedure.<sup>53</sup> Dimethylsulfide (Me<sub>2</sub>S, 280 μL, 3.78 mmol) was added quickly to a stirring solution of BI<sub>3</sub> (1.44 g, 3.67 mmol) in 10 mL of hexanes, resulting in the formation of a white crystalline precipitate after 1 minute. After stirring for 1 hour at room temperature, the precipitate was allowed to settle for 5 minutes and the mother liquor was subsequently decanted. Removal of the volatiles from the remaining solid afforded Me<sub>2</sub>S•BI<sub>3</sub> (1.08 g, 65 %). In addition, the decanted hexanes solution (mother liquor) was stored in the freezer (-30 °C) for 16 hours to afford colorless X-ray quality crystals of Me<sub>2</sub>S•BI<sub>3</sub>. <sup>1</sup>H NMR (699.7 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.44 – 1.45 (m, 6H, (H<sub>3</sub>C)<sub>2</sub>S). <sup>13</sup>C{<sup>1</sup>H} NMR (175.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 25.3 (s, (H<sub>3</sub>C)<sub>2</sub>S). <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ -68.5 (s, BI<sub>3</sub>).



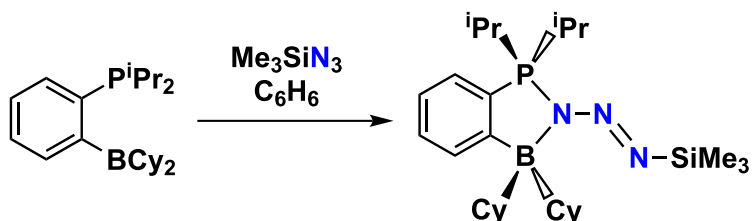
**Synthesis of PB{H(I)BNH<sub>2</sub>}:** A solution of Me<sub>2</sub>S•BI<sub>3</sub> (0.4361 g, 0.9624 mmol) in 2 mL of toluene was added to a solution of PB{H<sub>2</sub>BNH<sub>2</sub>} (0.3838 g, 0.9614 mmol) in 10 mL of toluene, resulting in the formation of a white precipitate. The reaction mixture was then stirred for 8 hours and the volatiles were removed under vacuum. The product was then washed with 3 x 2 mL of pentane, followed by the addition of 5 mL of benzene. The benzene solution was then frozen and placed under high vacuum to freeze-dry the product. Once the benzene was removed, 5 mL of hexanes was added and the mixture was filtered through a 2 cm plug of silica gel in a glass Pasteur pipette.

The filtrate was concentrated to a volume of 1 mL and cooled to  $-40\text{ }^{\circ}\text{C}$  for 16 hours to yield **PB{H(I)BNH<sub>2</sub>}** as colorless crystals of suitable quality for single crystal X-ray crystallography (0.1135 g, 22 % yield, 92 % purity by <sup>1</sup>H NMR spectroscopy). *Note: PB{H(I)BNH<sub>2</sub>}* could not be isolated in high enough purity to obtain suitable elemental analyses due to a persistent Me<sub>2</sub>S•Bl<sub>2</sub>H by-product that could not be removed. <sup>1</sup>H{<sup>11</sup>B} NMR (498.1 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.64 (dd, <sup>3</sup>J<sub>HP</sub> = 3.9 Hz, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 1H, ArCH), 7.20 – 7.24 (m, 1H, ArCH), 6.88 – 6.92 (m, 1H, ArCH), 6.74 – 6.78 (m, 1H, ArCH), 4.20 (br 1H, BH), 3.00 – 3.08 (m, 1H, NH), 2.78 (br s, 1H, NH), 2.66 (septet, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.98 (septet, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.76 – 1.89 (m, 8H, CyCH<sub>2</sub>), 1.62 – 1.69 (m, 1H, CyCH<sub>2</sub>), 1.44 – 1.53 (m, 1H, CyCH<sub>2</sub>), 1.32 – 1.39 (m, 6H, CyCH<sub>2</sub>), 1.18 – 1.28 (m, 2H, CyCH<sub>2</sub>), 1.15 (dd, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, <sup>3</sup>J<sub>HP</sub> = 8.5 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.90 – 0.97 (m, 1H, CyCH), 0.78 – 0.88 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.63 – 0.72 (m, 5H, CH(CH<sub>3</sub>)<sub>2</sub> & CyCH<sub>2</sub>), 0.46 – 0.52 (m, 1H, CyCH). <sup>13</sup>C{<sup>1</sup>H} NMR (175.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  134.9 (d, J<sub>CP</sub> = 14.6 Hz, ArCH), 130.6 (d, J<sub>CP</sub> = 2.6 Hz, ArCH), 130.4 (d, J<sub>CP</sub> = 4.9 Hz, ArCH), 124.0 (d, J<sub>CP</sub> = 8.6 Hz, ArCH), 117.6 (d, <sup>1</sup>J<sub>CP</sub> = 55.5 Hz, ArC), 34.8 (br, CyCH), 33.7 (br, CyCH), 31.9 (s, CyCH<sub>2</sub>), 31.8 (s, CyCH<sub>2</sub>), 31.3 (s, CyCH<sub>2</sub>), 30.4 (s, CyCH<sub>2</sub>), 30.3 (s, CyCH<sub>2</sub>), 29.6 (s, CyCH<sub>2</sub>), 29.4 (s, CyCH<sub>2</sub>), 28.3 (s, CyCH<sub>2</sub>), 28.1 (s, CyCH<sub>2</sub>), 24.1 (d, <sup>1</sup>J<sub>CP</sub> = 39.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 21.7 (d, <sup>1</sup>J<sub>CP</sub> = 41.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 17.6 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 17.1 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 17.0 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 15.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the resonance for the ArC bound to boron could not be located.* <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -8.0 (s, <sup>i</sup>Pr<sub>2</sub>P). <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -3.2 (br, BCy<sub>2</sub>, FWHM = 25 Hz), -21.9 (br, BH, FWHM = 55 Hz). Selected IR bands (Nujol mull, cm<sup>-1</sup>): 2730 (s, νB-H), 3271 (s, νN-H), 3314 (s, νN-H). m.p. 170 – 172 °C.

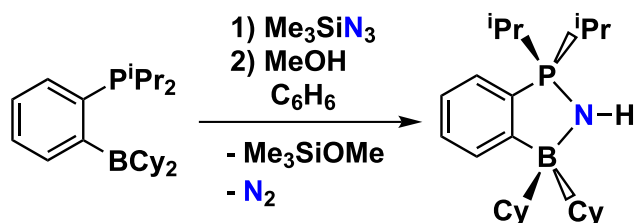


**Synthesis of PB{HBNH}**: A solution of K[N(SiMe<sub>3</sub>)<sub>2</sub>] (0.0214 g, 0.107 mmol) in 1 mL of toluene was added to a solution of **PB{H(I)BNH<sub>2</sub>}** (0.0563 g, 0.107 mmol) in 5 mL of toluene, resulting in the formation of a white precipitate. The reaction mixture was then stirred for 1 hour and the volatiles were removed under vacuum. 5 mL of hexanes was then added and the mixture was filtered through Celite. The filtrate was concentrated to a volume of 2 mL under vacuum and cooled to  $-40\text{ }^{\circ}\text{C}$  for 16 hours to yield **PB{HBNH}** as colorless crystals of suitable quality for single crystal X-ray crystallography (0.0205 g, 48 %). <sup>1</sup>H{<sup>11</sup>B} NMR (498.1 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.01 (dd, <sup>3</sup>J<sub>HP</sub> = 2.9 Hz, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 1H, ArCH), 7.29 – 7.33 (m, 1H, ArCH), 6.94 – 6.97 (m, 1H, ArCH), 6.80 – 6.84 (m, 1H, ArCH), 6.60 (br d, <sup>3</sup>J<sub>HP</sub> = 29.9 Hz, 1H, NH), 4.97 (br d, <sup>2</sup>J<sub>HP</sub> = 59.8 Hz, 1H, BH), 1.93 – 2.00 (m, 10H, CyCH<sub>2</sub>), 1.78 – 1.81 (m, 2H, CyCH<sub>2</sub>), 1.68 – 1.75 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.52 – 1.65 (m, 3H, CH(CH<sub>3</sub>)<sub>2</sub> and CyCH<sub>2</sub>), 1.35 – 1.42 (m, 2H, CyCH<sub>2</sub>), 1.19 – 1.28 (m, 2H, CyCH<sub>2</sub>), 0.82 – 0.95 (m, 4H, CyCH & CyCH<sub>2</sub>), 0.79 (dd, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, <sup>3</sup>J<sub>HP</sub> = 15.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.73 (dd, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, <sup>3</sup>J<sub>HP</sub> = 15.4 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (175.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  135.2 (d, J<sub>CP</sub> = 14.1 Hz, ArCH), 130.2 (d, J<sub>CP</sub> = 3.5 Hz, ArCH), 129.8 (d, J<sub>CP</sub> = 5.3 Hz, ArCH), 123.5 (d, J<sub>CP</sub> = 10.5 Hz, ArCH), 118.0 (d, <sup>1</sup>J<sub>CP</sub> = 65.0 Hz, ArC), 35.0 (br, CyCH), 31.8 (s, CyCH<sub>2</sub>), 31.0 (s, CyCH<sub>2</sub>), 30.3 (s, CyCH<sub>2</sub>), 30.2 (s, CyCH<sub>2</sub>), 28.8 (s,

CyCH<sub>2</sub>), 22.8 (d, <sup>1</sup>J<sub>CP</sub> = 40.4 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 17.8 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 17.6 (s, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the resonance for the ArC bound to boron could not be located.* <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ -11.8 (s, <sup>i</sup>Pr<sub>2</sub>P). <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ 28.2 (br s, BH, FWHM = 32 Hz), -5.8 (s, Cy<sub>2</sub>B). Selected IR bands (powder, KBr plate, cm<sup>-1</sup>): 2465 (s, νB-H), 3343 (s, νN-H), 1443 (s, νN=B). Anal. Calcd. for C<sub>24</sub>H<sub>42</sub>B<sub>2</sub>NP: C 72.57, H 10.66, N 3.53; Found: C 72.06, H 10.41, N 3.24. m.p. 118 – 120 °C.

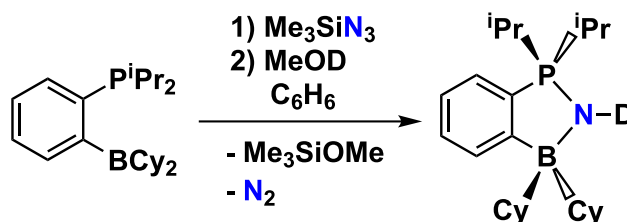


**Synthesis of PB{N<sub>3</sub>SiMe<sub>3</sub>}**: To a solution of PB<sup>S1</sup> (0.0239 g, 0.0645 mmol) in benzene (1 mL) was added Me<sub>3</sub>SiN<sub>3</sub> (8.6 μL, 0.065 mmol). The mixture was stirred for 1 hour, then the volatiles were removed under vacuum. The residue was dissolved in minimal pentane (*ca.* 1.25 mL) and placed in a -40 °C freezer for two days to obtain colorless crystals of PB{N<sub>3</sub>SiMe<sub>3</sub>} (0.0154 g, 49 %). <sup>1</sup>H NMR (499.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.89 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 1H, ArCH), 7.34 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 1H, ArCH), 6.95 – 7.05 (m, 2H, ArCH), 2.32 – 2.46 (m, 4H, CyCH<sub>2</sub> & CH(CH<sub>3</sub>)<sub>2</sub>), 1.83 – 2.12 (m, 8H, CyCH<sub>2</sub>), 1.46 – 1.65 (m, 10H, CyCH<sub>2</sub>), 1.12 – 1.20 (m, 2H, CyCH), 0.90 (dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>3</sup>J<sub>HP</sub> = 18.2 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.81 (dd, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>3</sup>J<sub>HP</sub> = 18.0 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.25 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>): δ 132.2 (d, J<sub>CP</sub> = 12.3 Hz, ArCH), 131.4 (d, J<sub>CP</sub> = 2.7 Hz, ArCH), 129.6 (d, J<sub>CP</sub> = 14.0 Hz, ArCH), 124.4 (d, J<sub>CP</sub> = 11.2 Hz, ArCH), 121.2 (d, <sup>1</sup>J<sub>CP</sub> = 94.8 Hz, ArC), 35.9 (br, CyCH), 32.7 (s, CyCH<sub>2</sub>), 31.9 (s, CyCH<sub>2</sub>), 30.4 (s, CyCH<sub>2</sub>), 30.4 (s, CyCH<sub>2</sub>), 28.8 (s, CyCH<sub>2</sub>), 27.8 (d, <sup>1</sup>J<sub>CP</sub> = 45.5 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 18.2 (d, <sup>2</sup>J<sub>CP</sub> = 2.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 17.3 (d, <sup>2</sup>J<sub>CP</sub> = 1.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), -1.2 (s, Si(CH<sub>3</sub>)<sub>3</sub>). *Note: the resonance for the ArC bound to boron could not be located.* <sup>31</sup>P{<sup>1</sup>H} NMR (201.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 55.5 (s, <sup>i</sup>Pr<sub>2</sub>P). <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.5 (s, BCy<sub>2</sub>). Anal. Calcd. for C<sub>27</sub>H<sub>49</sub>BN<sub>3</sub>PSi: C 66.79, H 10.17, N 8.65; Found: C 66.66, H 10.21, N 8.37. m.p. 104.5 °C (dec.).

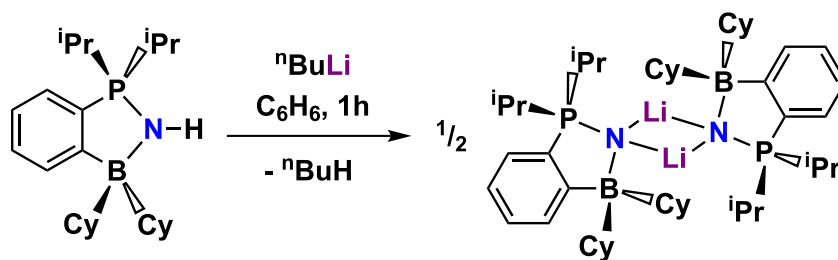


**Synthesis of PB{NH}**: Neat Me<sub>3</sub>SiN<sub>3</sub> (179 μL, 0.135 mmol) was added dropwise to a solution of PB<sup>S1</sup> (0.500 g, 1.35 mmol) in benzene (10 mL) and left to stir for one hour. Methanol (55 μL, 1.4 mmol, wet/reagent grade) was then added dropwise, causing rapid evolution of N<sub>2</sub> gas. Ten minutes after effervescence subsided, the volatiles were removed under vacuum to yield PB{NH} as a colorless air- and moisture-stable solid (0.489 g, 94 %). Crystals suitable for X-ray diffraction were obtained from a saturated mixture of hexanes/dichloromethane at -40 °C. *Note: bulk recrystallization is possible in 4:1 hexanes:dichloromethane at -35 °C, but is typically unnecessary.*

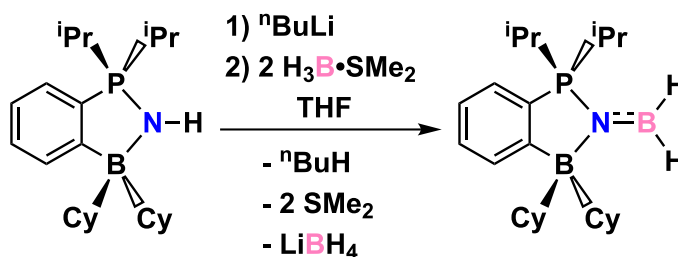
$^1\text{H}$  NMR (499.8 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.83 (d,  $^3J_{\text{HH}} = 7.5$  Hz, 1H, ArCH), 7.31 (pseudo t,  $^3J_{\text{HH}} = 7.1$  Hz, 1H, ArCH), 7.02 (dd,  $^3J_{\text{HH}} = 7.0$ ,  $^3J_{\text{HP}} = 12.7$  Hz, 1H, ArCH), 6.95 (pseudo t,  $^3J_{\text{HH}} = 7.6$  Hz, 1H, ArCH), 2.18 (d,  $^3J_{\text{HH}} = 12.6$  Hz, 2H, CyCH<sub>2</sub>), 2.07 (d,  $^3J_{\text{HH}} = 12.5$  Hz, 2H, CyCH<sub>2</sub>), 1.99 (t,  $^3J_{\text{HH}} = 12.3$  Hz, 4H, CyCH<sub>2</sub>), 1.76 (d,  $^3J_{\text{HH}} = 12.7$  Hz, 2H, CyCH<sub>2</sub>), 1.42 – 1.72 (m, 8H, CyCH<sub>2</sub> & CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (dq,  $^3J_{\text{HH}} = 2.7$  Hz,  $^3J_{\text{HH}} = 12.6$  Hz, 2H, CyCH<sub>2</sub>), 1.18 (dq,  $^3J_{\text{HH}} = 2.9$  Hz,  $^3J_{\text{HH}} = 12.5$  Hz, 2H, CyCH<sub>2</sub>), 0.93 (t,  $^3J_{\text{HH}} = 12.2$  Hz, 2H, CyCH), 0.64 – 0.76 (m, 13H, NH & CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the NH resonance overlaps the CH(CH<sub>3</sub>)<sub>2</sub> resonance at 0.64 – 0.76 ppm, see NMR data for PB{ND}*.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.7 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  131.9 (d,  $J_{\text{CP}} = 14.5$  Hz, ArCH), 130.8 (d,  $J_{\text{CP}} = 2.9$  Hz, ArCH), 127.3 (d,  $J_{\text{CP}} = 17.5$  Hz, ArCH), 126.1 (d,  $^1J_{\text{CP}} = 107.6$  Hz, ArC), 124.4 (d,  $J_{\text{CP}} = 12.6$  Hz, ArCH), 34.7 (br, CyCH), 32.6 (s, CyCH<sub>2</sub>), 32.2 (s, CyCH<sub>2</sub>), 30.4 (s, CyCH<sub>2</sub>), 30.2 (s, CyCH<sub>2</sub>), 28.9 (s, CyCH<sub>2</sub>), 26.9 (d,  $^1J_{\text{CP}} = 52.5$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 17.0 (d,  $^2J_{\text{CP}} = 2.3$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 16.4 (d,  $^2J_{\text{CP}} = 2.1$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the resonance for the ArC bound to boron could not be located.*  $^{31}\text{P}\{^1\text{H}\}$  NMR (201.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  61.6 (s,  $^i\text{Pr}_2\text{P}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (159.8 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.7 (s, BCy<sub>2</sub>). Selected IR bands ( $\text{CH}_2\text{Cl}_2$  dropcast,  $\text{cm}^{-1}$ ): 3431 (m,  $\nu\text{N-H}$ ). Anal. Calcd. for  $\text{C}_{24}\text{H}_{41}\text{BNP}$ : C 74.80, H 10.72, N 3.63; Found: C 74.22, H 10.35, N 3.63. m.p. 170 – 171 °C.



**Synthesis of PB{ND}**: Neat  $\text{Me}_3\text{SiN}_3$  (12.4  $\mu\text{L}$ , 0.0934 mmol) was added to a solution of **PB** (0.0347 g, 0.0937 mmol) in benzene (1.5 mL) and left to stir for one hour. Deuterated methanol (4  $\mu\text{L}$ , 0.1 mmol) was then added. After stirring for one hour, the volatiles were removed under vacuum to give **PB{ND}** as a colorless solid (0.0333 g, 92 %).  $^1\text{H}$  NMR (498.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.84 (d,  $^3J_{\text{HH}} = 7.4$  Hz, 1H, ArCH), 7.31 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 1H, ArCH), 7.00 – 7.06 (m, 1H, ArCH), 6.96 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 1H, ArCH), 2.19 (d,  $^3J_{\text{HH}} = 12.7$  Hz, 2H, CyCH<sub>2</sub>), 2.07 (d,  $^3J_{\text{HH}} = 12.5$  Hz, 2H, CyCH<sub>2</sub>), 2.00 (t,  $^3J_{\text{HH}} = 12.4$  Hz, 4H, CyCH<sub>2</sub>), 1.77 (d,  $^3J_{\text{HH}} = 12.7$  Hz, 2H, CyCH<sub>2</sub>), 1.40 – 1.74 (m, 8H, CyCH<sub>2</sub> & CH(CH<sub>3</sub>)<sub>2</sub>), 1.32 (dq,  $^3J_{\text{HH}} = 3.2$  Hz,  $^3J_{\text{HH}} = 12.5$  Hz, 2H, CyCH<sub>2</sub>), 1.19 (dq,  $^3J_{\text{HH}} = 3.4$  Hz,  $^3J_{\text{HH}} = 12.6$  Hz, 2H, CyCH<sub>2</sub>), 0.94 (t,  $^3J_{\text{HH}} = 12.2$  Hz, 2H, CyCH), 0.73 (dd,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HP}} = 10.2$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.70 (dd,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HP}} = 10.6$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>).  $^2\text{H}$  NMR (61.4 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.73 (s, ND).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.7 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  132.0 (d,  $J_{\text{CP}} = 14.5$  Hz, ArCH), 130.8 (d,  $J_{\text{CP}} = 2.9$  Hz, ArCH), 127.3 (d,  $J_{\text{CP}} = 17.4$  Hz, ArCH), 126.1 (d,  $^1J_{\text{CP}} = 107.5$  Hz, ArC), 124.5 (d,  $J_{\text{CP}} = 12.6$  Hz, ArCH), 34.7 (br, CyCH), 32.6 (s, CyCH<sub>2</sub>), 32.2 (s, CyCH<sub>2</sub>), 30.4 (s, CyCH<sub>2</sub>), 30.2 (s, CyCH<sub>2</sub>), 28.9 (s, CyCH<sub>2</sub>), 26.9 (d,  $^1J_{\text{CP}} = 52.5$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 17.0 (d,  $^2J_{\text{CP}} = 2.3$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 16.4 (d,  $^2J_{\text{CP}} = 2.2$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the resonance for the ArC bound to boron could not be located.*  $^{31}\text{P}\{^1\text{H}\}$  NMR (201.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  61.5 (s,  $^i\text{Pr}_2\text{P}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128.27 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.6 (s, BCy<sub>2</sub>). Selected IR bands (powder, KBr plate,  $\text{cm}^{-1}$ ): 2542 (m,  $\nu\text{N-D}$ ). m.p. 146 – 148 °C.

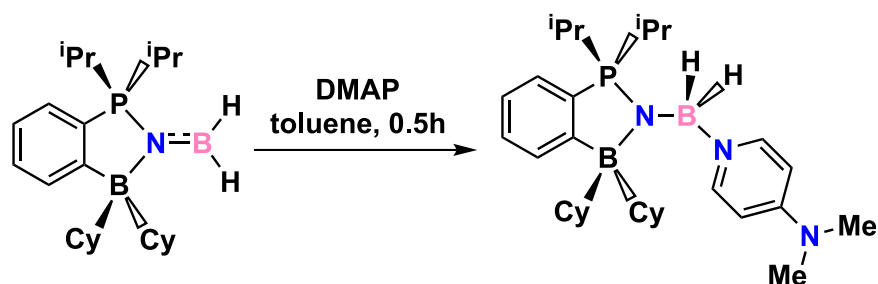


**Synthesis of [PB{NLi}]<sub>2</sub>:** To a solution of PB{NH} (0.0571 g, 0.148 mmol) in benzene (2 mL), <sup>n</sup>BuLi (65 μL, 0.16 mmol, 2.5 M solution in hexanes) was added dropwise and the resulting solution was stirred for one hour. The volatiles were removed under vacuum, and the resulting yellow residue was dissolved in 4 mL of 3:1 hexanes:toluene, then placed in a -40 °C freezer. After one week, the mother liquor was decanted away to obtain colorless crystals of [PB{NLi}]<sub>2</sub> (0.0090 g, 16 %). Colorless needle-like crystals suitable for X-ray diffraction were grown from a saturated hexanes solution at -40 °C. *Note: this reaction proceeds quantitatively, and so it is often more convenient to generate [PB{NLi}]<sub>2</sub> in situ; due to its high reactivity toward hydrolysis, isolated samples of [PB{NLi}]<sub>2</sub> are occasionally contaminated with PB{NH}.* <sup>1</sup>H NMR (499.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.90 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, ArCH), 7.38 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, ArCH), 7.18 – 7.23 (m, 2H, ArCH), 7.11 – 7.15 (m, 2H, ArCH), 2.22 – 2.33 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.06 – 2.15 (m, 4H, CyCH<sub>2</sub>), 1.93 – 2.02 (m, 4H, CyCH<sub>2</sub>), 1.74 – 1.88 (m, 8H, CyCH<sub>2</sub>), 1.20 – 1.59 (m, 20H, CyCH<sub>2</sub>), 1.15 (dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>3</sup>J<sub>HP</sub> = 14.4 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (dd, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>3</sup>J<sub>HP</sub> = 14.4 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.99 – 1.08 (m, 4H, CyCH<sub>2</sub>), 0.74 – 0.83 (m, 4H, CyCH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>): δ 132.0 (d, J<sub>CP</sub> = 17.1 Hz, ArCH), 129.2 (d, J<sub>CP</sub> = 30.8 Hz, ArCH), 127.5 (d, J<sub>CP</sub> = 6.2 Hz, ArCH), 124.3 (d, J<sub>CP</sub> = 9.3 Hz, ArCH), 35.9 (br, CyCH), 33.3 (s, CyCH<sub>2</sub>), 33.1 (s, CyCH<sub>2</sub>), 30.3 (d, <sup>1</sup>J<sub>CP</sub> = 55.5 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 29.8 (s, CyCH<sub>2</sub>), 29.5 (s, CyCH<sub>2</sub>), 28.1 (s, CyCH<sub>2</sub>), 18.7 (d, <sup>2</sup>J<sub>CP</sub> = 11.2 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the ArC resonances bound to boron and phosphorus could not be located.* <sup>31</sup>P{<sup>1</sup>H} NMR (201.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 60.1 (s, iPr<sub>2</sub>P). <sup>11</sup>B{<sup>1</sup>H} NMR (159.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ 4.5 (s, BCy<sub>2</sub>). <sup>7</sup>Li{<sup>1</sup>H} NMR (155.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.4 (s, NLi). Anal. Calcd. for C<sub>48</sub>H<sub>80</sub>B<sub>2</sub>Li<sub>2</sub>N<sub>2</sub>P<sub>2</sub>: C 73.67, H 10.30, N 3.58; Found: C 74.16, H 10.66, N 3.43. m.p. 140 °C (dec.).



**Synthesis of PB{NBH<sub>2</sub>}:** To a solution of PB{NH} (0.1529 g, 0.3968 mmol) in THF (10 mL) was added <sup>n</sup>BuLi (158.7 μL, 0.40 mmol, 2.5 M solution in hexanes) dropwise. The resulting solution was stirred for one hour, then a solution of Me<sub>2</sub>S·BH<sub>3</sub> (396.8 μL, 0.79 mmol, 2.0 M solution in THF) was added dropwise, and the mixture was left stirring for 15 minutes. The volatiles were removed under vacuum, and the residue was extracted into hexanes (2 × 10 mL). The solvent volume was reduced to ca. 1 mL under vacuum, and the mixture was placed in a -40 °C freezer overnight. After decanting away the mother liquor and drying the remaining solid under vacuum,

**PB{NBH<sub>2</sub>}** was obtained as a white powder (0.1131 g, 72 %). Crystals suitable for X-ray diffraction were grown from a saturated hexanes solution at -40 °C. <sup>1</sup>H{<sup>31</sup>P} NMR (400.0 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.89 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 1H, ArCH), 7.32 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 1H, ArCH), 7.00 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 1H, ArCH), 6.93 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 1H, ArCH), 5.66 (s, 1H, BH<sub>2</sub>), 5.31 (s, 1H, BH<sub>2</sub>), 1.83 – 2.14 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub> & CyCH<sub>2</sub>), 1.38 – 1.59 (m, 8H, CyCH<sub>2</sub>) 1.29 (dq, <sup>3</sup>J<sub>HH</sub> = 2.6 Hz, <sup>3</sup>J<sub>HH</sub> = 12.3 Hz, 2H, CyCH<sub>2</sub>), 1.03 – 1.14 (m, 2H, CyCH), 0.78 (dd, <sup>3</sup>J<sub>HH</sub> = 4.3 Hz, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 132.4 (d, J<sub>CP</sub> = 14.8 Hz, ArCH), 131.7 (d, J<sub>CP</sub> = 2.9 Hz, ArCH), 127.5 (d, J<sub>CP</sub> = 16.4 Hz, ArCH), 125.0 (d, J<sub>CP</sub> = 12.0 Hz, ArCH), 123.8 (d, J<sub>CP</sub> = 101.9 Hz, ArC), 35.1 (br, CyCH), 32.2 (s, CyCH<sub>2</sub>), 31.6 (s, CyCH<sub>2</sub>), 30.4 (s, CyCH<sub>2</sub>), 30.2 (s, CyCH<sub>2</sub>), 28.7 (s, CyCH<sub>2</sub>), 27.6 (d, J<sub>CP</sub> = 49.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 16.5 (d, J<sub>CP</sub> = 7.2 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 16.5 (d, J<sub>CP</sub> = 6.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the resonance for the ArC bound to boron could not be located.* <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 68.0 (s, iPr<sub>2</sub>P). <sup>11</sup>B NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ 45.9 (br s, FWHM = 820.5 Hz, BH<sub>2</sub>), 4.7 (s, BCy<sub>2</sub>). *Note: B–H coupling was not observed in the BH<sub>2</sub> resonance due to the large peak width.* Selected IR bands (CH<sub>2</sub>Cl<sub>2</sub> dropcast, cm<sup>-1</sup>): 2540 (m, νB-H, sym), 2455 (m, νB-H, asym), 1342 (s, νN=B). Anal. Calcd. for C<sub>24</sub>H<sub>42</sub>B<sub>2</sub>NP: C 72.57, H 10.66, N 3.53; Found: C 71.80, H 10.77, N 3.40. *Note: the difference between the calculated and found values for C likely stems from incomplete combustion of the sample.* m.p. 82 °C (dec.).



**Synthesis of PB{NBH<sub>2</sub>}•DMAP:** To a solution of **PB{NBH<sub>2</sub>}** (0.0385 g, 0.0969 mmol) in toluene (2 mL), was added dropwise a solution of 4-dimethylaminopyridine (0.0123, 0.101 mmol) in toluene (2 mL) over one minute. The resulting solution was stirred for 30 minutes, then the volatiles were removed under vacuum. After washing the remaining solid with hexanes (1 mL) and drying under vacuum, **PB{NBH<sub>2</sub>}•DMAP** was obtained as a white powder (0.0400 g, 79 %). Crystals suitable for X-ray crystallography were grown from a saturated solution of hexanes/dichloromethane at -40 °C. <sup>1</sup>H{<sup>31</sup>P} NMR (400.0 MHz, C<sub>6</sub>D<sub>6</sub>): δ 8.38 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, ArCH in DMAP), 8.05 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H, ArCH), 7.42 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 1H, ArCH), 7.26 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz 1H, ArCH), 7.13 (d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz 1H, ArCH), 5.79 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, ArCH in DMAP), 4.05 (br, 2H, BH<sub>2</sub>), 2.52 – 2.66 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.05 – 2.20 (m, 4H, CyCH<sub>2</sub>), 1.90 – 2.06 (m, 12H, N(CH<sub>3</sub>)<sub>2</sub> & CyCH<sub>2</sub>), 1.71 – 1.85 (m, 2H, CyCH<sub>2</sub>), 1.48 – 1.64 (m, 4H, CyCH<sub>2</sub>), 1.30 – 1.47 (m, 4H, CyCH<sub>2</sub>), 1.27 (d, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (d, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.80 – 0.99 (m, 2H, CyCH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>): δ 155.1 (s, ArC in DMAP) 146.6 (s, ArCH in DMAP), 132.3 (d, J<sub>CP</sub> = 14.7 Hz, ArCH), 129.5 (d, J<sub>CP</sub> = 2.7 Hz, ArCH), 128.8 (d, J<sub>CP</sub> = 50.0 Hz, ArC), 127.5 (d, J<sub>CP</sub> = 15.0 Hz, ArCH), 123.7 (d, J<sub>CP</sub> = 11.0 Hz, ArCH), 106.0 (s, ArCH in DMAP), 38.3 (s, N(CH<sub>3</sub>)<sub>2</sub>), 35.9 (br, CyCH), 32.9 (s, CyCH<sub>2</sub>), 32.6 (s, CyCH<sub>2</sub>), 30.9 (s, CyCH<sub>2</sub>), 30.8 (s, CyCH<sub>2</sub>), 29.3 (d, J<sub>CP</sub> = 42.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 29.2 (s, CyCH<sub>2</sub>), 18.6 (d, J<sub>CP</sub> = 2.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 18.3 (d, J<sub>CP</sub> = 1.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). *Note: the resonance for the ArC bound to boron*



could not be located.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.9 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  56.9 (s,  $^i\text{Pr}_2\text{P}$ ).  $^{11}\text{B}$  NMR (128.3 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.3 (s,  $\text{BCy}_2$ ), -1.4 (s,  $\text{BH}_2$ ). Note: B–H coupling was not observed in the  $\text{BH}_2$  resonance. Anal. Calcd. for  $\text{C}_{31}\text{H}_{52}\text{B}_2\text{N}_3\text{P}$ : C 71.69, H 10.09, N 8.09; Found: C 70.66, H 10.02, N 7.90. Note: the difference between the calculated and found values for C likely stems from incomplete combustion of the sample. m.p. 144 – 145 °C.

### 3. Single Crystal X-Ray Structure Determinations

Appropriate X-ray quality crystals were coated with a small amount of hydrocarbon oil (Paratone-N) and removed from the glovebox in a vial. A crystal was then quickly mounted onto a loop and placed in a low temperature stream of nitrogen on the X-ray diffractometer. All data was collected using a Bruker APEX II CCD detector on a D8 Duo or PLATFORM diffractometer using  $\text{Mo K}\alpha$  (0.71073 Å) or  $\text{Cu K}\alpha$  (1.54178 Å) radiation. The data was corrected for absorption through Gaussian integration from the indexing of crystal faces.<sup>54</sup> Crystal structures were solved using intrinsic phasing (SHELXT) and refined using SHELXL.<sup>55</sup> For **PB{N<sub>3</sub>SiMe<sub>3</sub>}**, **PB{NH}**, **[PB{NLi}]<sub>2</sub>**, **PB{NBH<sub>2</sub>}**, and **PB{NBH<sub>2</sub>}•DMAP**, Olex2 was used as a GUI.<sup>56</sup> The assignment of carbon-bound hydrogen atom positions are based on the  $\text{sp}^2$ - or  $\text{sp}^3$ -hybridization geometries of their attached carbon atoms and were given thermal parameters 20 % greater than those of their parent atoms. Molecular structures are shown with thermal ellipsoids at a 50 % probability level and have been imaged using Diamond.<sup>57</sup> All crystal structures were deposited into the Cambridge Crystallographic Data Centre (CCDC) database 2106474–2106482.

**Table S1** Crystallographic data for **PB{H<sub>2</sub>BNH<sub>2</sub>}**, **PB{H(I)BNH<sub>2</sub>}**, and **PB{HBNH}**.

Compound	<b>PB{H<sub>2</sub>BNH<sub>2</sub>}</b> <sup>b</sup>	<b>PB{H(I)BNH<sub>2</sub>}</b> <sup>b</sup>	<b>PB{HBNH}</b> <sup>b</sup>
Formula	C <sub>24</sub> H <sub>44</sub> B <sub>2</sub> NP	C <sub>27</sub> H <sub>50</sub> B <sub>2</sub> NPI	C <sub>24</sub> H <sub>42</sub> B <sub>2</sub> NP
Formula weight	399.19	568.17	397.17
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i> (No.14)	<i>P2<sub>1</sub>/c</i> (No. 14)	<i>P2<sub>1</sub>/c</i> (No. 14)
Crystal dimensions (mm)	0.29×0.18×0.10	0.12×0.05×0.04	0.27×0.27×0.13
<i>a</i> (Å)	19.7455(6)	18.2679(5)	11.1624(4)
<i>b</i> (Å)	10.9680(3)	11.4128(4)	9.3546(3)
<i>c</i> (Å)	23.1511(7)	14.6131(4)	23.6269(8)
$\alpha$ (°)	90	90	90
$\beta$ (°)	102.217(2)	107.048(2)	99.5776(19)
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	4900.3(3)	2912.78(15)	2432.73(14)
<i>Z</i>	8	4	4
$\rho$ (g/cm <sup>3</sup> )	1.082	1.296	1.084
Abs coeff (mm <sup>-1</sup> )	1.032	9.241	1.039
Radiation	Cu K $\alpha$	Cu K $\alpha$	Cu K $\alpha$
<i>T</i> (°C)	-100	-100	-100
2 $\theta$ <sub>max</sub> (°)	148.42	147.90	145.55
Total data	112848	38672	92836
Unique data ( <i>R</i> <sub>int</sub> )	9929 (0.1008)	5714 (0.1170)	4766 (0.0584)
Obs data [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	7806	4015	4438
Restraints/Parameters	0/545	2/276 <sup>c,d</sup>	0/261
<i>R</i> <sub>1</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0432	0.0539	0.0519
w <i>R</i> <sub>2</sub> [all data] <sup>a</sup>	0.1175	0.1380	0.1376
Max/min $\Delta\rho$ (e <sup>-</sup> Å <sup>-3</sup> )	0.390/-0.330	1.238/-0.995	0.605 <sup>e</sup> /-0.231

$${}^aR_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^4)]^{1/2}.$$

<sup>b</sup>Hydrogen atoms bound to boron or nitrogen were located in the difference maps and refined isotropically; all other H atoms were placed in idealized positions and refined using a riding model.

<sup>c</sup>Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent hexane atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in *PLATON* (A. L. Spek, *Acta Cryst. C*, 2015, **71**, 9–18). A total solvent-accessible void volume of 444 Å<sup>3</sup> with a total electron count of 107 (consistent with 2 molecules of solvent hexane, or 0.5 molecules per formula unit of **PB{H(I)BNH<sub>2</sub>}**) was found in the unit cell.

<sup>d</sup>The bond lengths of N–H1N and N–H2N are restrained to be similar by *SHELXL* command SADI.

<sup>e</sup>The largest peak (0.605 e<sup>-</sup> Å<sup>-3</sup>) in the difference map was located 1.5 Å from C21 (of a cyclohexyl group) and likely arises from a small amount of unresolved disorder of the Cy group (atoms C21 to C26). Given that the largest U<sub>eq</sub> for any of the carbon atoms in that Cy group was only 0.072

and that there were no anomalies with the bond distances or angles, it was decided that it was not worth pursuing a highly restrained/constrained disorder model for that group.

**Table S2** Crystallographic data for **PB{N<sub>3</sub>SiMe<sub>3</sub>}**, **PB{NH}**, and **[PB{N(Li)}]<sub>2</sub>**.

Compound	<b>PB{N<sub>3</sub>SiMe<sub>3</sub>}</b>	<b>PB{NH}</b> <sup>b</sup>	<b>[PB{N(Li)}]<sub>2</sub></b> <sup>c,d</sup>
Formula	C <sub>27</sub> H <sub>49</sub> BN <sub>3</sub> PSi	C <sub>24</sub> H <sub>41</sub> BNP	C <sub>57</sub> H <sub>101</sub> B <sub>2</sub> Li <sub>2</sub> N <sub>2</sub> P <sub>2</sub>
Formula weight	485.56	385.36	911.83
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>Pn</i> (No.7)	<i>P2<sub>1</sub>/c</i> (No.14)	<i>P</i> $\bar{1}$ (No.2)
Crystal dimensions (mm)	0.27×0.20×0.19	0.18×0.10×0.09	0.43×0.09×0.04
<i>a</i> (Å)	9.4802(3)	10.5379(3)	10.7171(3)
<i>b</i> (Å)	10.2175(8)	9.6520(3)	16.7686(5)
<i>c</i> (Å)	15.3118(11)	22.5624(6)	17.2773(6)
$\alpha$ (°)	90	90	68.428(2)
$\beta$ (°)	99.8940(10)	92.7034(12)	75.826(2)
$\gamma$ (°)	90	90	77.713(2)
<i>V</i> (Å <sup>3</sup> )	1461.10(19)	2290.5(2)	2773.46(16)
<i>Z</i>	2	4	2
$\rho$ (g/cm <sup>3</sup> )	1.104	1.117	1.092
Abs coeff (mm <sup>-1</sup> )	0.154	1.096	0.966
Radiation	Mo K $\alpha$	Cu K $\alpha$	Cu K $\alpha$
<i>T</i> (°C)	-100	-80	-80
2 $\theta$ <sub>max</sub> (°)	54.974	145.51	140.84
Total data	26386	60334	10288
Unique data ( <i>R</i> <sub>int</sub> )	6671 (0.0302)	4544 (0.0450)	10288 (0.1088)
Obs data [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	6306	4140	7944
Restraints/Parameters	2/305	0/252	49 <sup>e</sup> /530
<i>R</i> <sub>1</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0301	0.0345	0.0765
w <i>R</i> <sub>2</sub> [all data] <sup>a</sup>	0.0755	0.0956	0.2176
Max/min $\Delta\rho$ (e <sup>-</sup> Å <sup>-3</sup> )	0.24/-0.12	0.28/-0.27	0.602/-0.826

$$^aR_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}.$$

<sup>b</sup>Hydrogen atoms bound to boron or nitrogen were located in the difference maps and refined isotropically; all other H atoms were placed in idealized positions and refined using a riding model.

<sup>c</sup>The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program *CELL\_NOW* (Bruker AXS Inc., Madison, WI, 2004). The second twin component can be related to the first component by 180° rotation about the [-0.282 -0.339 1] axis in real space and about the [0 0 1] axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a *SHELXL-2014* HKLF 5 reflection file with the data integration program *SAINTE* (version V8.38A), using all

reflection data (exactly overlapped, partially overlapped and non-overlapped). The refined value of the twin fraction (*SHELXL-2014* BASF parameter) was 0.394(2).

<sup>d</sup>Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent hexanes carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in *PLATON* (A. L. Spek, *Acta Cryst. C*, 2015, **71**, 9–18). A total solvent-accessible void volume of 631 Å<sup>3</sup> with a total electron count of 139 (consistent with 1.5 molecules of solvent hexane, or 0.75 molecules per formula unit of **[PB{NLi}]<sub>2</sub>**) was found in the unit cell.

<sup>e</sup>Two isopropyl groups (one attached to P1 and the other attached to P2) were found to exhibit rotational disorder about their respective P-C bonds. In both cases the disorder could be adequately modelled by two parts with the minor component rotated by approximately 180° relative to that of the major orientation. The C–C distances within the disordered isopropyl groups were restrained to be approximately the same by use of the *SHELXL* SADI instruction. Further, the rigid bond restraint (RIGU) was also applied to the disordered isopropyl groups. Finally, pairs of atoms (eg C14 & C14A, C15 & C15A, etc) were constrained to have equivalent anisotropic displacement parameters. Refined occupancies of 0.667(7) and 0.333(7) for isopropyl group C14 to C16 and C14A to C16A and refined occupancies of 0.639(8) and 0.361(8) for isopropyl group C51 to C53 and C51A to C53A.

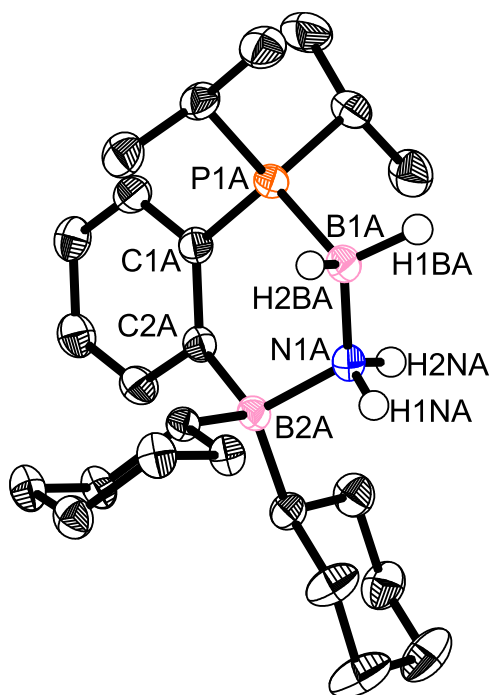
**Table S3** Crystallographic data for **PB{NBH<sub>2</sub>}**, **PB{NBH<sub>2</sub>}•DMAP**, and **Me<sub>2</sub>S•BI<sub>3</sub>**.

Compound	<b>PB{NBH<sub>2</sub>}</b> <sup>b</sup>	<b>PB{NBH<sub>2</sub>}•DMAP</b> <sup>b</sup>	<b>Me<sub>2</sub>S•BI<sub>3</sub></b>
Formula	C <sub>24</sub> H <sub>42</sub> B <sub>2</sub> NP	C <sub>32</sub> H <sub>54</sub> B <sub>2</sub> N <sub>3</sub> P <sub>2</sub> Cl <sub>2</sub> <sup>c</sup>	C <sub>2</sub> H <sub>6</sub> BSI <sub>3</sub>
Formula weight	397.17	604.27	453.64
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/n</i> (No. 14)	<i>P</i> $\bar{1}$ (No.2)	<i>P2<sub>1</sub>/c</i> (No.14)
Crystal dimensions (mm)	0.38×0.23×0.15	0.19×0.17×0.09	0.07×0.06×0.11
<i>a</i> (Å)	11.6992(12)	9.5926(12)	7.0765(4)
<i>b</i> (Å)	9.8865(10)	11.0351(14)	7.2293(3)
<i>c</i> (Å)	21.0275(19)	16.641(2)	18.9898(9)
$\alpha$ (°)	90	98.954(2)	90
$\beta$ (°)	90.527(2)	98.334(2)	92.749(2)
$\gamma$ (°)	90	99.920(2)	90
<i>V</i> (Å <sup>3</sup> )	2432.0(4)	1687.1(4)	970.36(8)
<i>Z</i>	4	2	4
$\rho$ (g/cm <sup>3</sup> )	1.085	1.189	3.105
Abs coeff (mm <sup>-1</sup> )	0.123	0.266	77.20
Radiation	Mo K $\alpha$	Mo K $\alpha$	Cu K $\alpha$
<i>T</i> (°C)	-100	-100	-100
2 $\theta$ <sub>max</sub> (°)	58.714	54.358	149.46
Total data	15541	30383	37103
Unique data ( <i>R</i> <sub>int</sub> )	6374 (0.0399)	7484 (0.0498)	1973 (0.0628)
Obs data [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	4547	5428	1912
Restraints/Parameters	0/265	0/403	0/67
<i>R</i> <sub>1</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0630	0.0430	0.0297
<i>wR</i> <sub>2</sub> [all data] <sup>a</sup>	0.1808	0.1116	0.0787
Max/min $\Delta\rho$ (e <sup>-</sup> Å <sup>-3</sup> )	0.70/-0.45	0.31/-0.34	1.551/-1.295

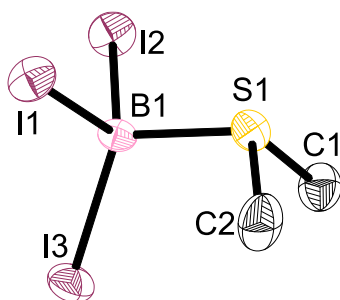
$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}.$$

<sup>b</sup>Hydrogen atoms bound to boron or nitrogen were located in the difference maps and refined isotropically; all other H atoms were placed in idealized positions and refined using a riding model.

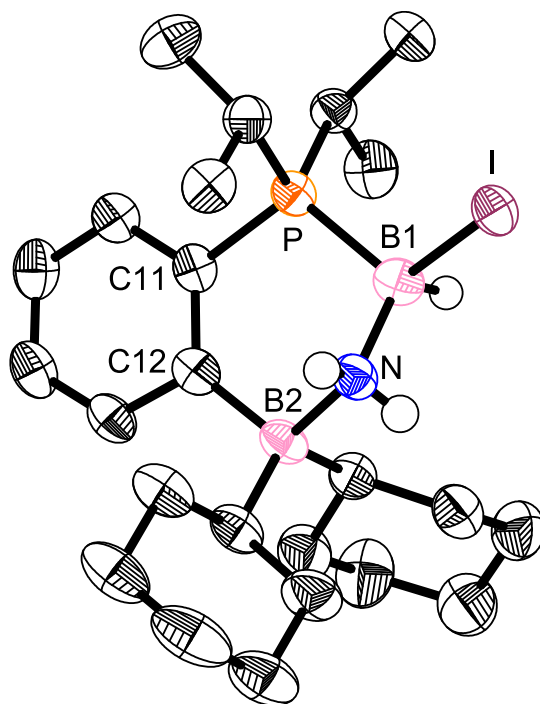
<sup>c</sup>The unit cell contains 2 molecules of disordered dichloromethane, equal to 1 molecule per formula unit of **PB{NBH<sub>2</sub>}•DMAP**. The disordered dichloromethane was modelled in two parts with refined occupancies of 0.609(18) and 0.391(18).



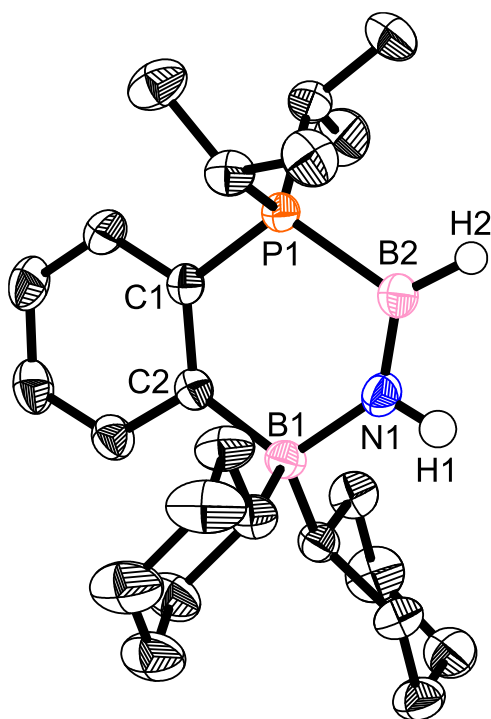
**Fig. S1** Molecular structure of  $\text{PB}\{\text{H}_2\text{BNH}_2\}$  with thermal ellipsoids plotted at 50 % probability. Unit cell contains two molecules (A and B); only molecule A is shown above. All carbon-bound hydrogen atoms have been omitted for clarity. H atoms bound to boron and nitrogen were located in the difference Fourier maps and isotropically refined. Selected bond lengths [Å] and angles [°] for molecules A and [B]: P1–C1 1.8022(16) [1.8019(16)], P1–B1 1.9418(19) [1.9425(19)], N1–B1 1.573(2) [1.574(2)], N1–B2 1.630(2) [1.626(2)], C2–B2 1.649(2) [1.650(2)], N1–H1N 0.95(2) [0.89(2)], N1–H2N 0.91(2) [0.88(2)], B1–H1B 1.17(2) [1.145(19)], B2–H2B 1.122(19) [1.139(19)]; C1–P1–B1 111.76(7) [111.71(7)], B1–N1–B2 120.45(12) [120.98(12)], B1–N1–H1N 108.3(12) [106.8(12)], B2–N1–H1N 104.5(12) [105.8(13)], B1–N1–H2N 110.1(13) [109.5(14)], B2–N1–H2N 108.0(13) [109.5(14)].



**Fig. S2** Molecular structure of  $\text{Me}_2\text{S}\cdot\text{BI}_3$  with thermal ellipsoids plotted at 50 % probability. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: I1–B1 2.232(5), I2–B1 2.219(5), I3–B1 2.212(5), S1–C1 1.803(6), S1–B1 1.937(6); C1–S1–C2 100.8(3), C1–S1–B1 105.2(3), S1–B1–I2 104.5(2).

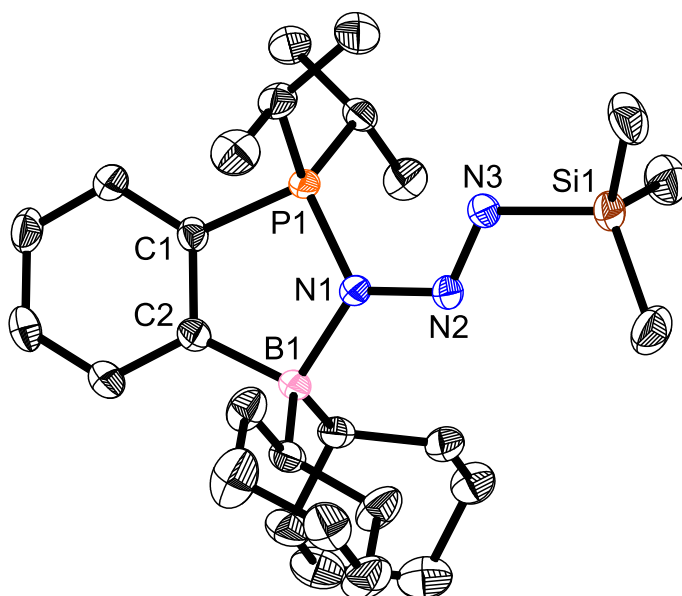


**Fig. S3** Molecular structure of  $\text{PB}\{\text{H}(\text{I})\text{BNH}_2\}$  with thermal ellipsoids plotted at 50 % probability. All carbon-bound hydrogen atoms have been omitted for clarity. The H atoms bound to boron and nitrogen were located in the difference Fourier maps and isotropically refined. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: P–C11 1.807(5), P–B1 1.944(7), I–B1 2.290(7), N–B1 1.523(7), N–B2 1.657(8), C12–B2 1.633(8); C11–P–B1 107.5(3), B1–N–B2 118.1(4), I–B1–P 110.7(3), I–B1–N 109.9(4), P–B1–N 109.2(4), N–B2–C12 109.1(4).

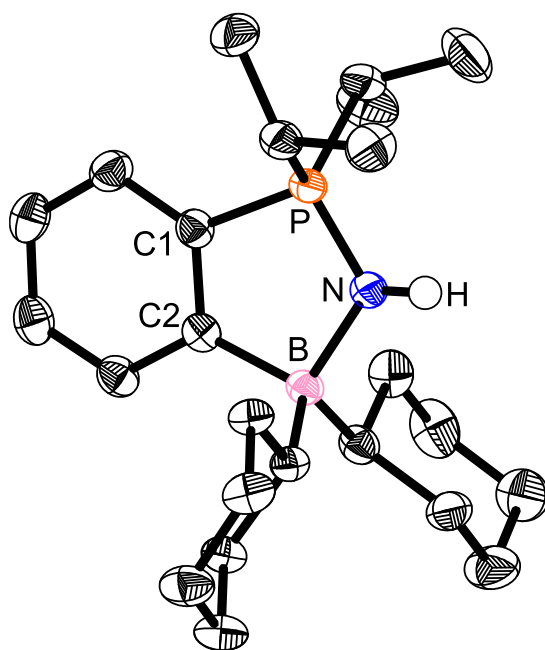


**Fig. S4** Molecular structure of **PB{HBNH}** with thermal ellipsoids plotted at 50 % probability. All carbon-bound hydrogen atoms have been omitted for clarity; H1 and H2 were located in the difference Fourier maps and isotropically refined. Selected bond lengths [Å] and angles [°]: P1–C1 1.7945(18), P1–B2 1.927(2), B2–N1 1.347(3), B2–H2 1.13(2), N1–H1 0.88(3), B1–N1 1.579(3), B1–C2 1.645(3); C1–P1–B2 108.35(9), N1–B1–C2 111.29(14), B1–N1–B2 133.91(17), P1–B2–N1 114.80(15).

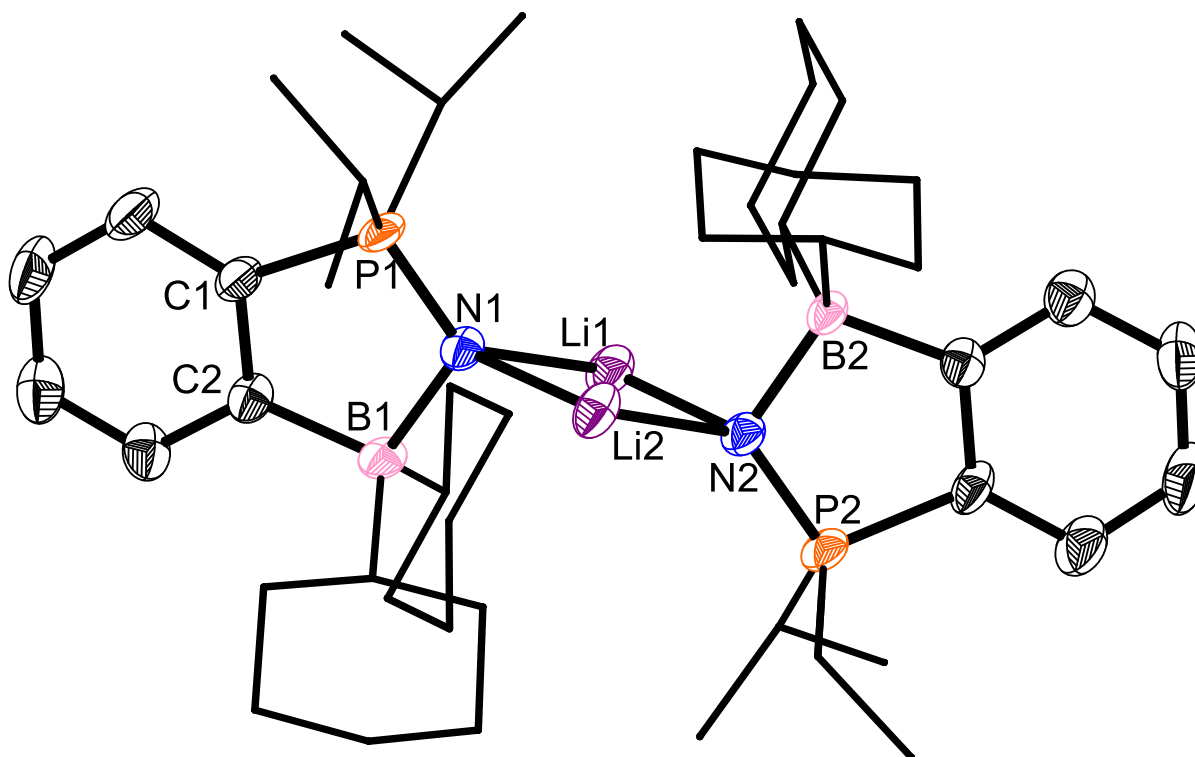




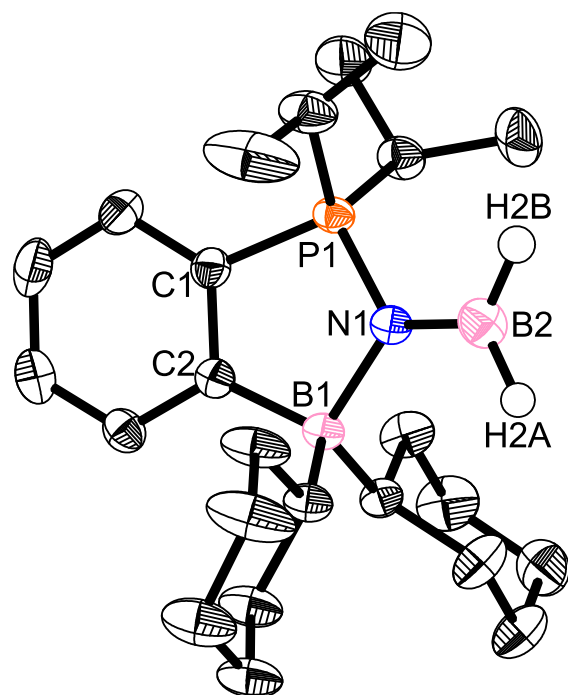
**Fig. S5** Molecular structure of **PB{N<sub>3</sub>SiMe<sub>3</sub>}** with thermal ellipsoids plotted at 50 % probability. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.788(2), P1–N1 1.6875(17), N1–N2 1.347(2), N2–N3 1.264(2), N3–Si1 1.7884(19), B1–N1 1.624(3), B1–C2 1.620(3); N1–P1–C1 93.85(9), B1–N1–P1 117.61(13), C2–B1–N1 98.54(15), N3–N2–N1 113.58(17), N2–N3–Si1 114.47(14).



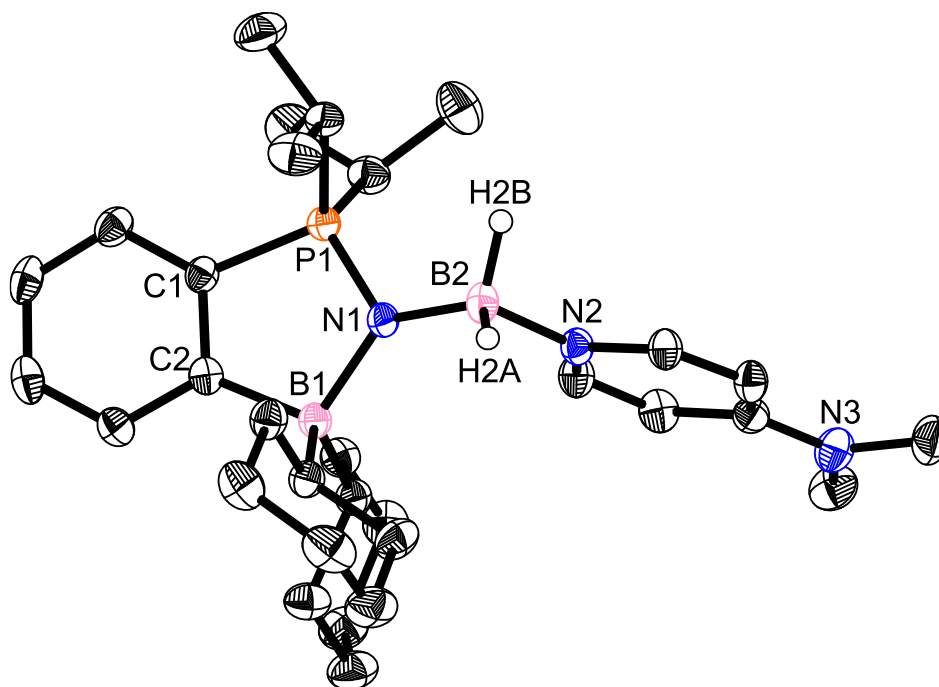
**Fig. S6** Molecular structure of **PB{NH}** with thermal ellipsoids plotted at 50 % probability. All carbon-bound hydrogen atoms have been omitted for clarity. H was located in the difference Fourier maps and isotropically refined. Selected bond lengths [Å] and angles [°]: P–C1 1.7839(12), P–N 1.6092(10), N–H 0.833(17), B–N 1.6223(15), B–C2 1.6318(16); N–P–C1 97.66(5), P–N–B 115.97(7), N–B–C2 99.57(8), P–N–H 118.5(12), B–N–H 124.1(12).



**Fig. S7** Molecular structure of  $[\text{PB}\{\text{NLi}\}]_2$  with thermal ellipsoids plotted at 50 % probability. All hydrogen atoms have been omitted for clarity; isopropyl and cyclohexyl groups are shown in wireframe; only the major orientation of the disordered isopropyl groups is shown. Selected interatomic distances [Å] and bond angles [°]: P1–C1 1.799(4), P1–N1 1.589(3), N1–Li1 2.017(7), N1–Li2 1.975(7), N1–B1 1.654(5), B1–C2 1.631(5); N1–P1–C1 102.97(16), P1–N1–B1 110.1(2), N1–B1–C2 103.8(3), P1–N1–Li1 128.7(3), P1–N1–Li2 130.7(3), Li1–N1–Li2 69.8(3), B1–N1–Li1 96.9(3), B1–N1–Li2 111.8(3), N1–Li1–N2 108.4(3).



**Fig. S8** Molecular structure of  $\text{PB}\{\text{NBH}_2\}$  with thermal ellipsoids plotted at 50 % probability. All carbon-bound hydrogen atoms have been omitted for clarity. H2A and H2B were located in the difference Fourier maps and isotropically refined Selected bond lengths [Å] and angles [°]: P1–C1 1.777(2), P1–N1 1.6538(16), N1–B1 1.659(3), N1–B2 1.396(3), B2–H2A 1.13(3), B1–C2 1.630(3); N1–P1–C1 98.92(9), P1–N1–B1 112.56(12), B2–N1–P1 121.47(16), H2A–B2–N1 118.9(13), C2–B1–N1 100.71(14); torsion angle H2A–B2–N1–P1 178.8(15).



**Fig. S9** Molecular structure of **PB{NBH<sub>2</sub>}•DMAP** with thermal ellipsoids plotted at 50 % probability. All carbon-bound hydrogen atoms and one molecule of dichloromethane have been omitted for clarity. H2A and H2B were located in the difference Fourier maps and isotropically refined. Selected bond lengths [Å] and angles [°]: P1–C1 1.7910(16), P1–N1 1.6125(14), N1–B1 1.643(2), N1–B2 1.527(2), B2–H2A 1.125(17), B2–N2 1.663(2), B1–C2 1.633(2); N1–P1–C1 100.21(7), P1–N1–B1 112.84(10), B2–N1–P1 117.34(12), N1–B2–N2 113.79(14), H2A–B2–N1 113.7(8), C2–B1–N1 101.40(13).

## 4. NMR Spectra

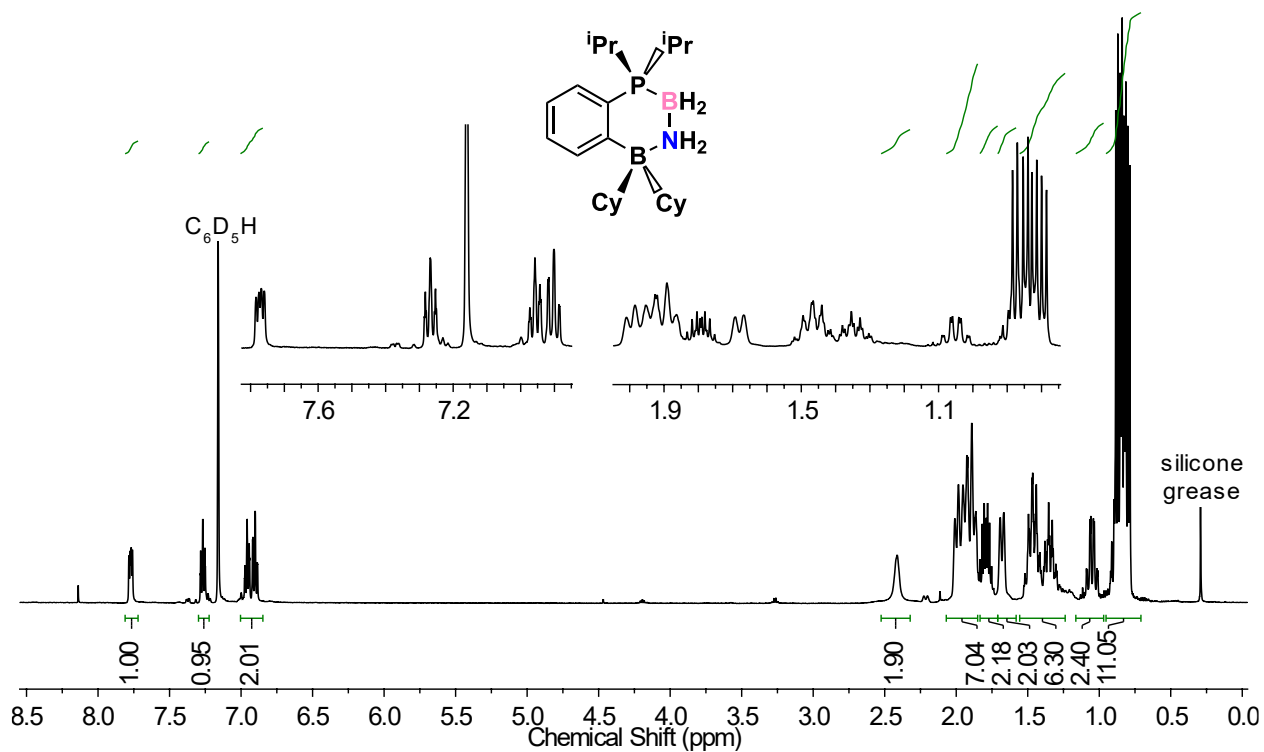


Fig. S10  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of  $\text{PB}\{\text{H}_2\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

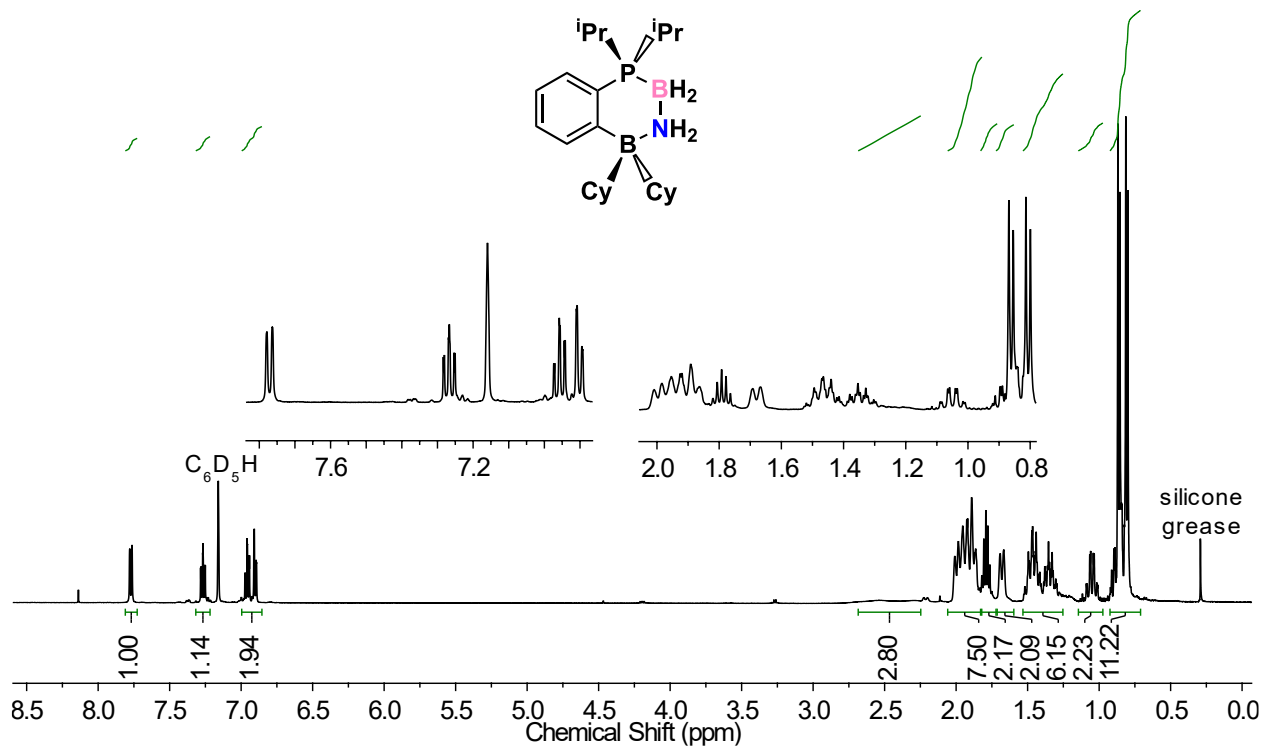


Fig. S11  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum of  $\text{PB}\{\text{H}_2\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

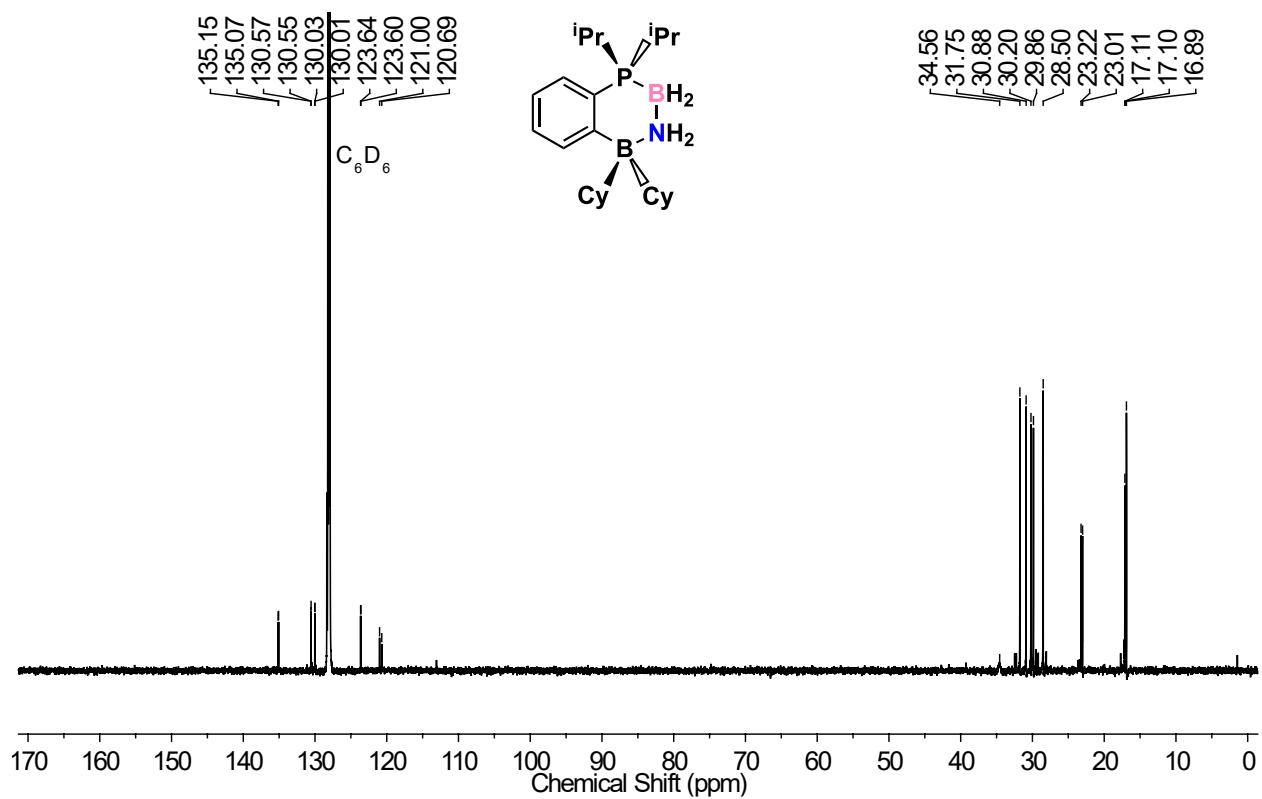


Fig. S12  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{H}_2\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

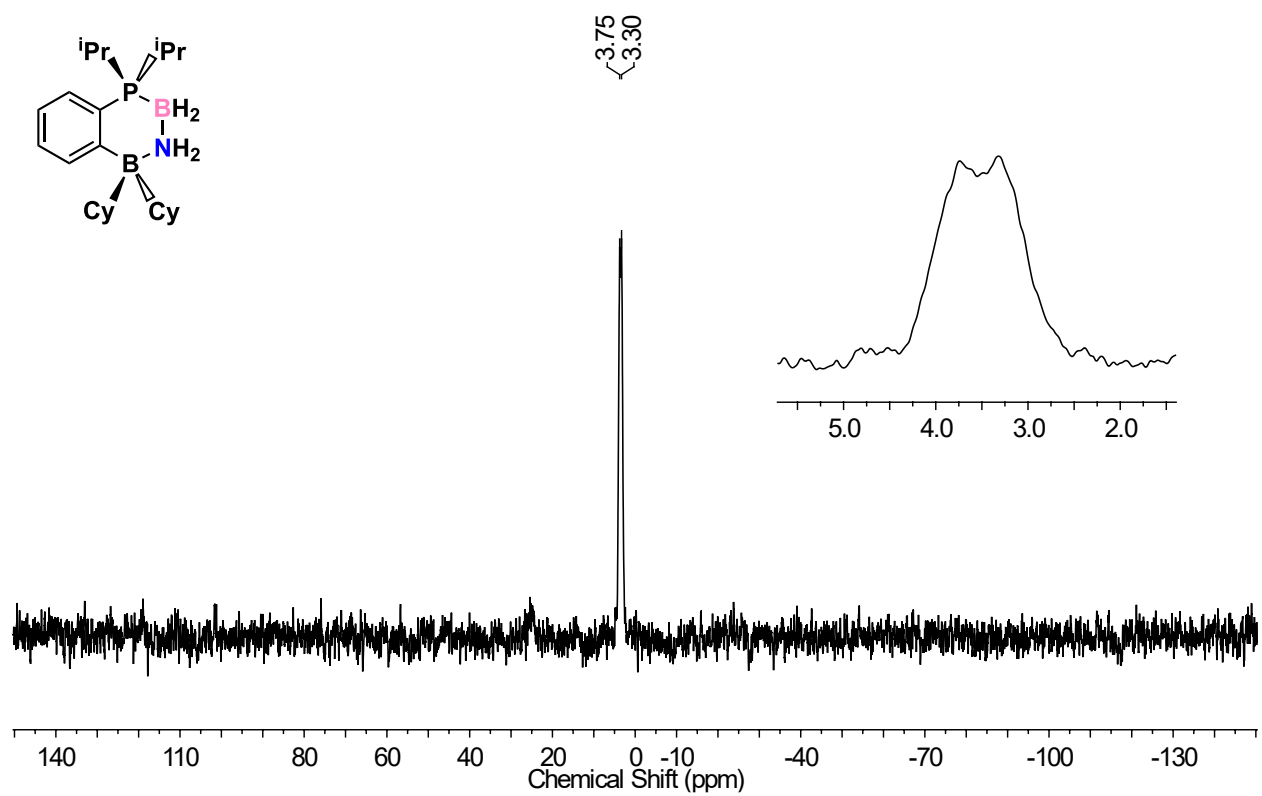


Fig. S13  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{H}_2\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

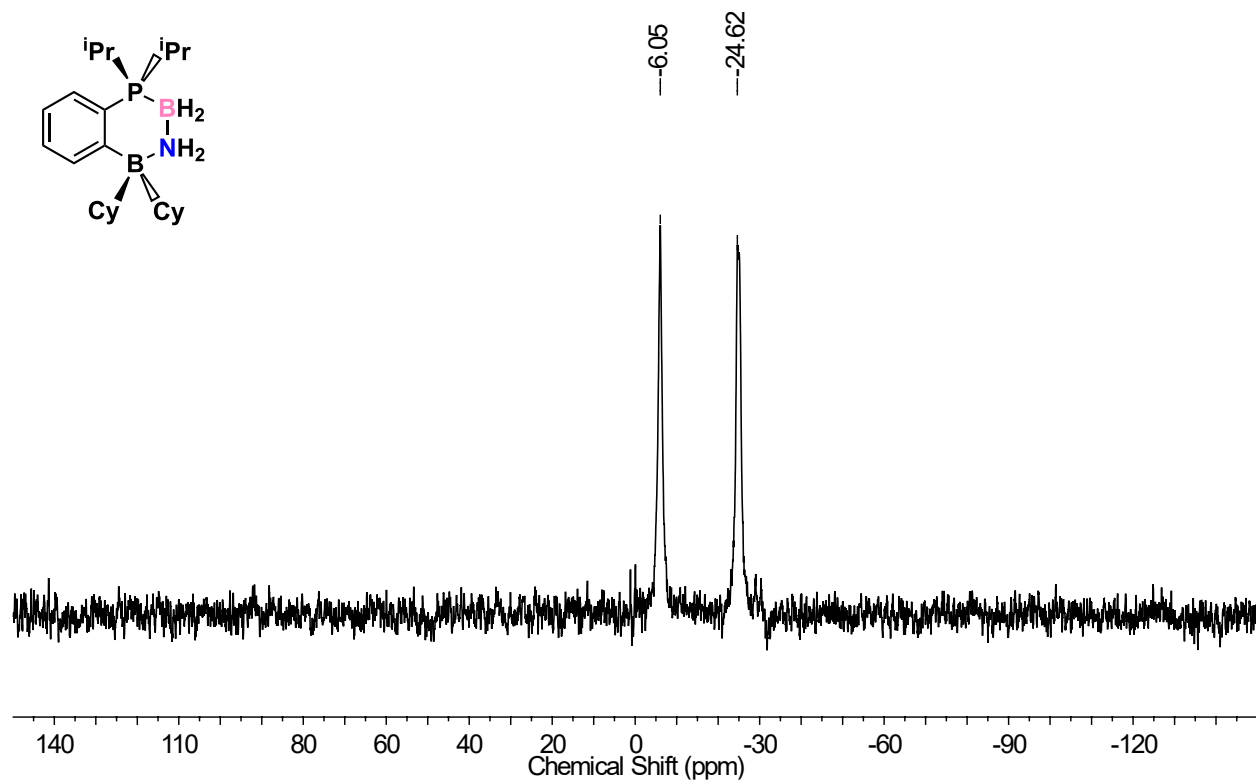


Fig. S14  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{H}_2\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

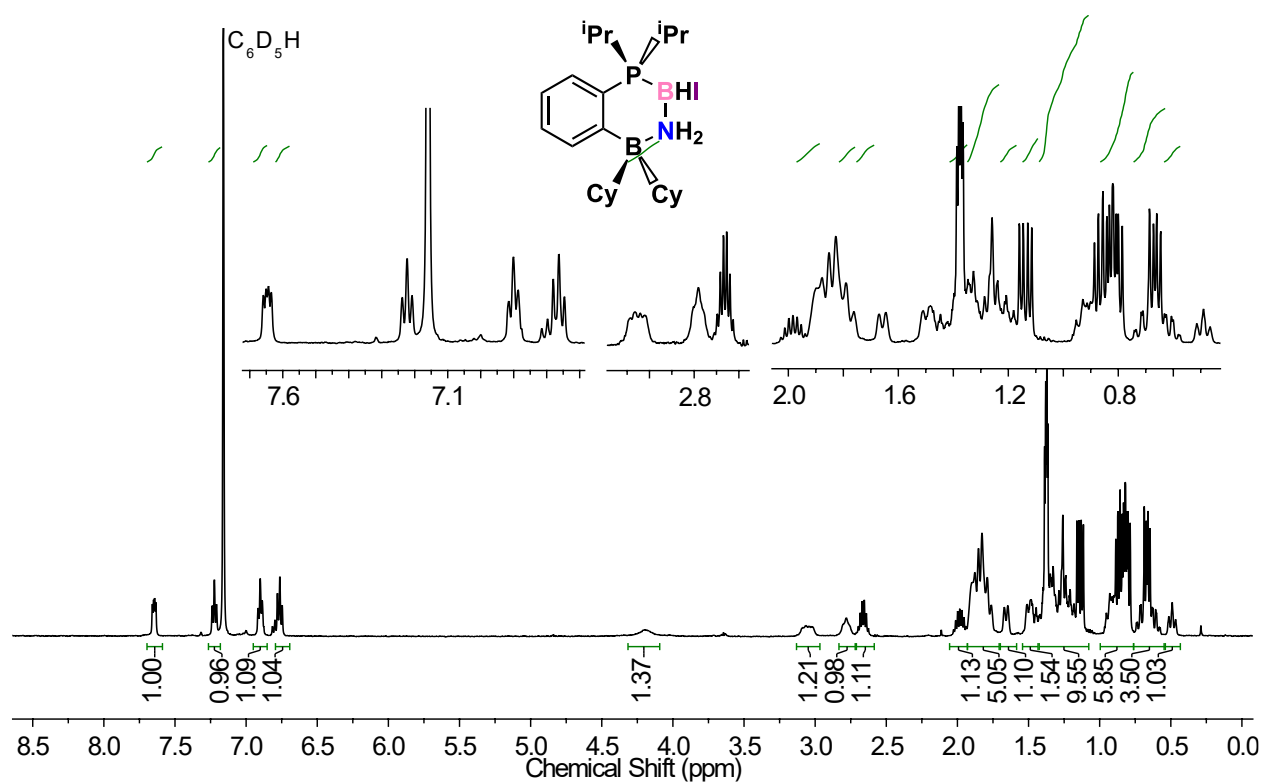


Fig. S15  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of  $\text{PB}\{\text{H}(\text{I})\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

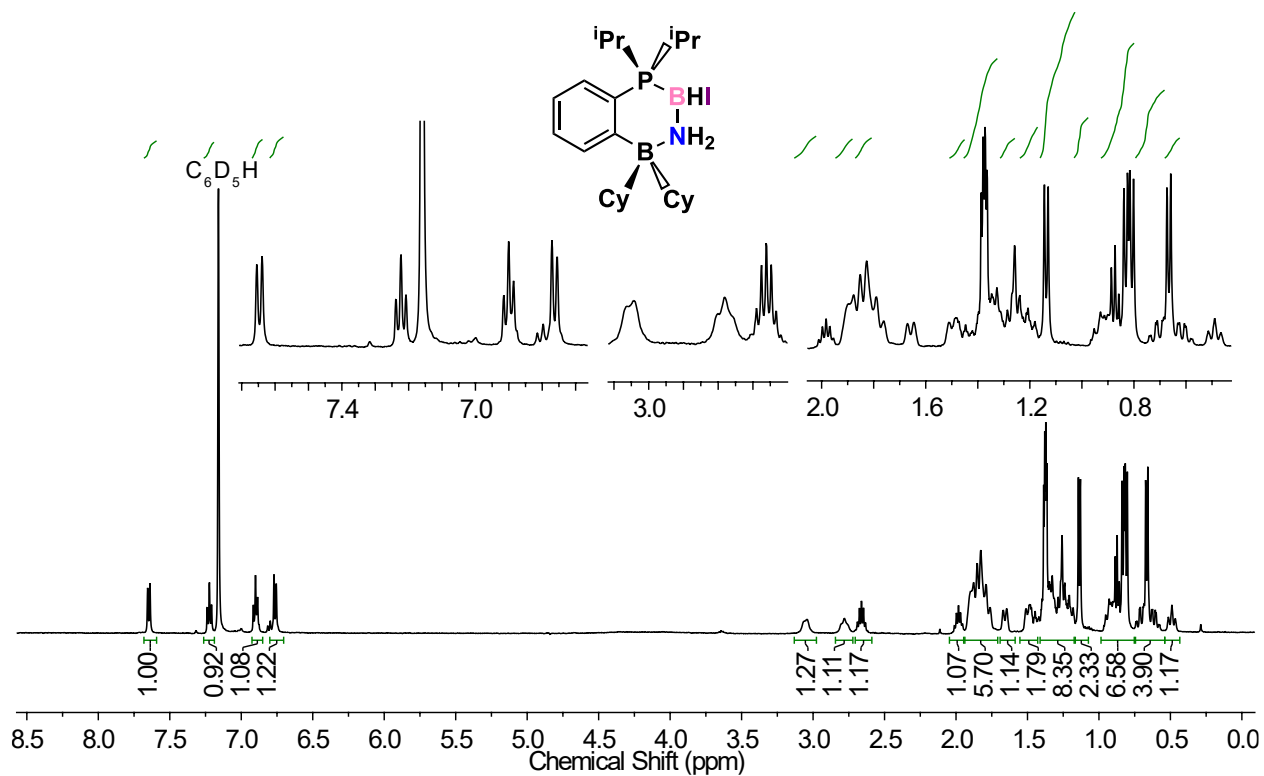


Fig. S16  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum of  $\text{PB}\{\text{H}(\text{I})\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

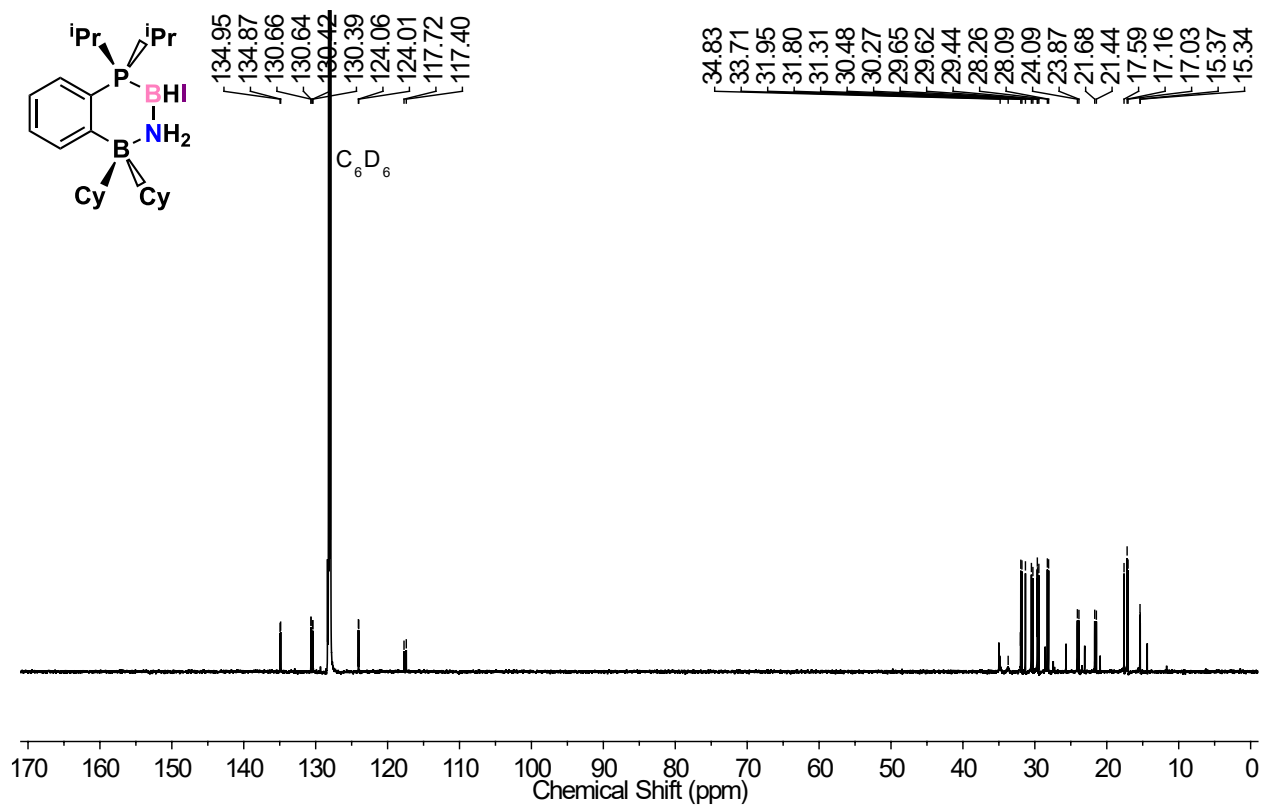


Fig. S17  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{H}(\text{I})\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .



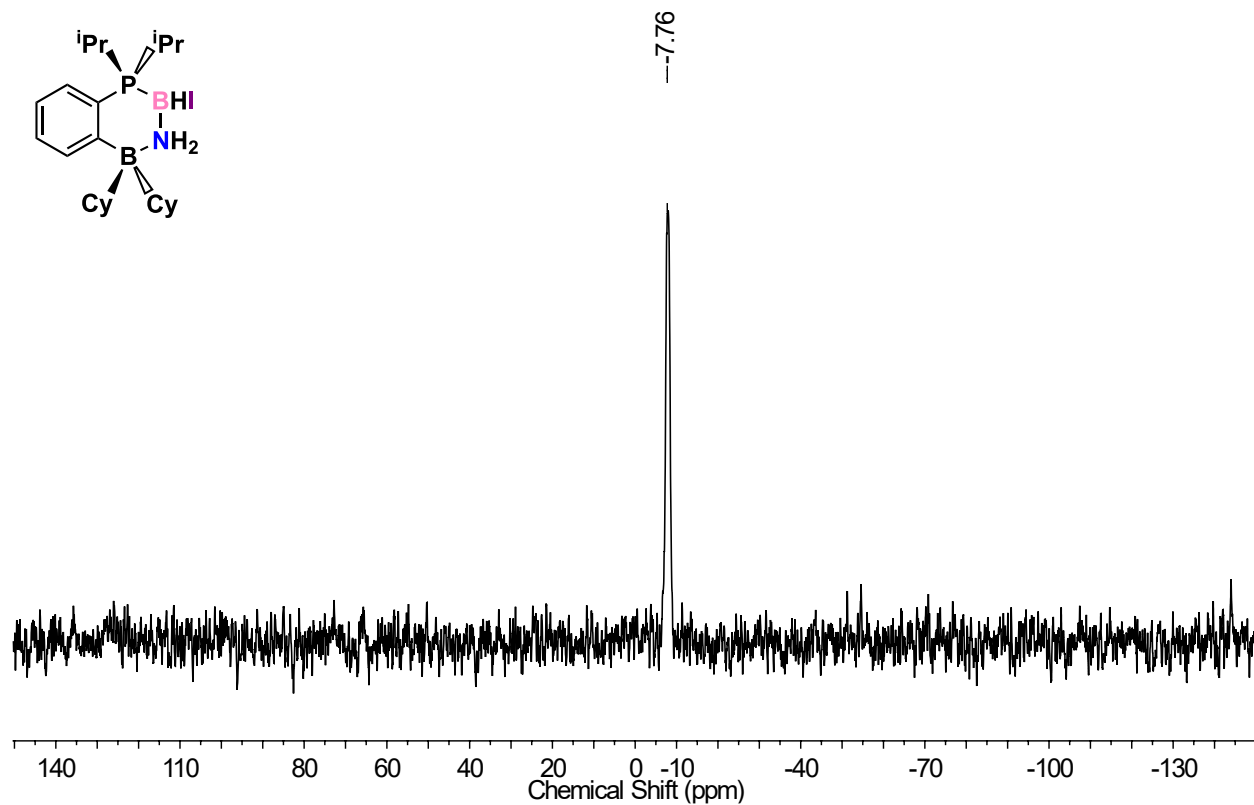


Fig. S18  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{H}(\text{I})\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

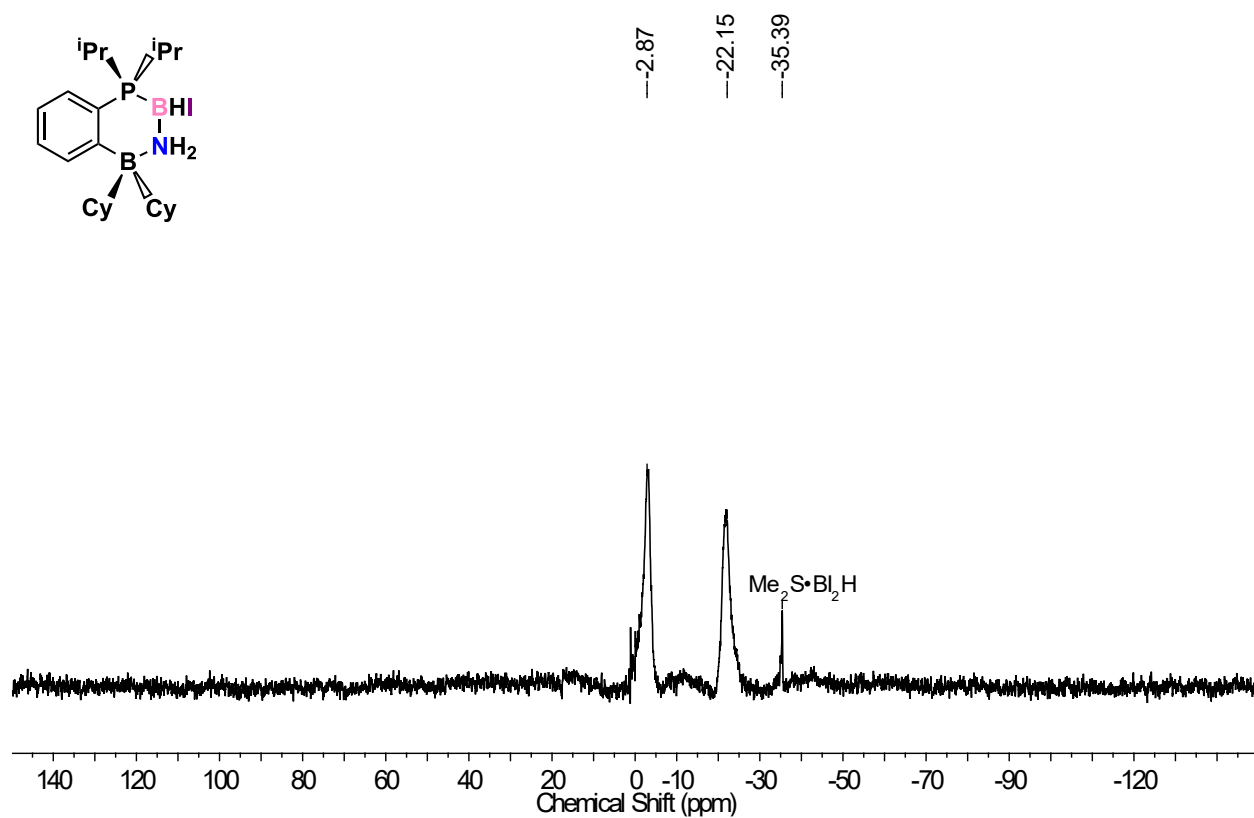


Fig. S19  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{H}(\text{I})\text{BNH}_2\}$  in  $\text{C}_6\text{D}_6$ .

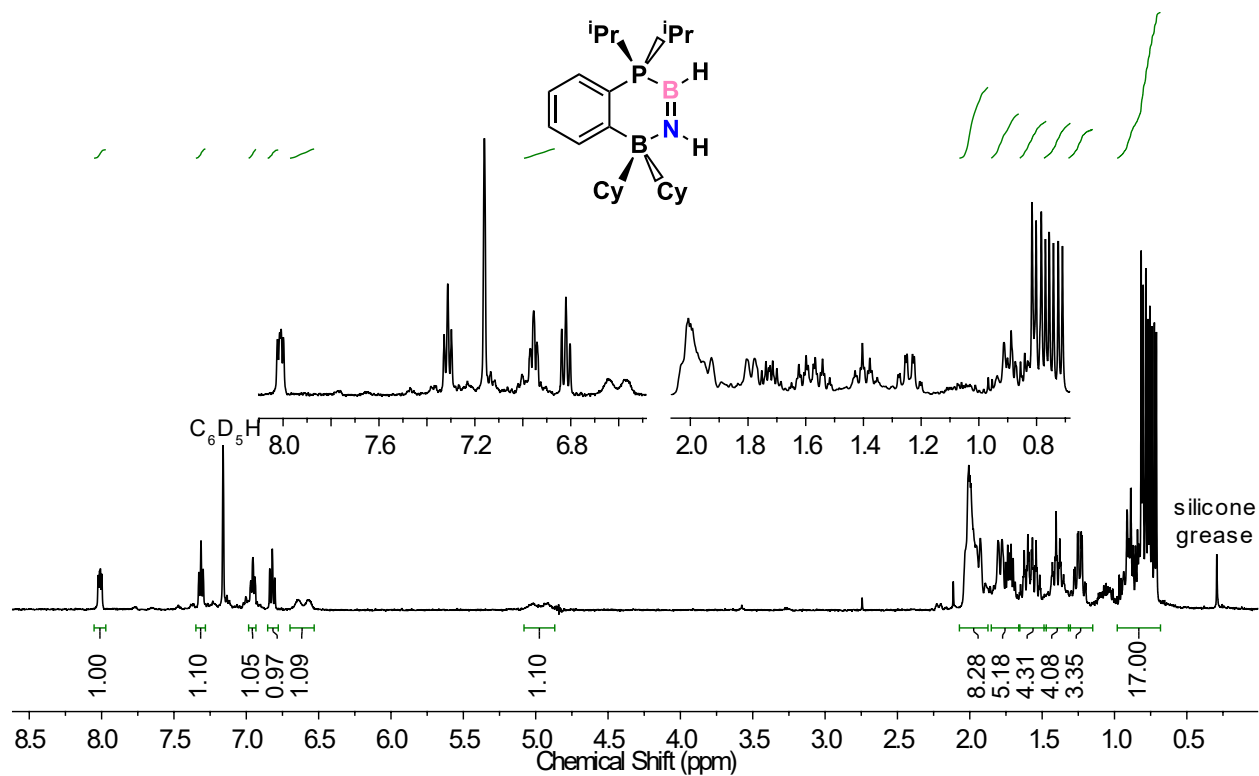


Fig. S20  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of  $\text{PB}\{\text{HBNH}\}$  in  $\text{C}_6\text{D}_6$ .

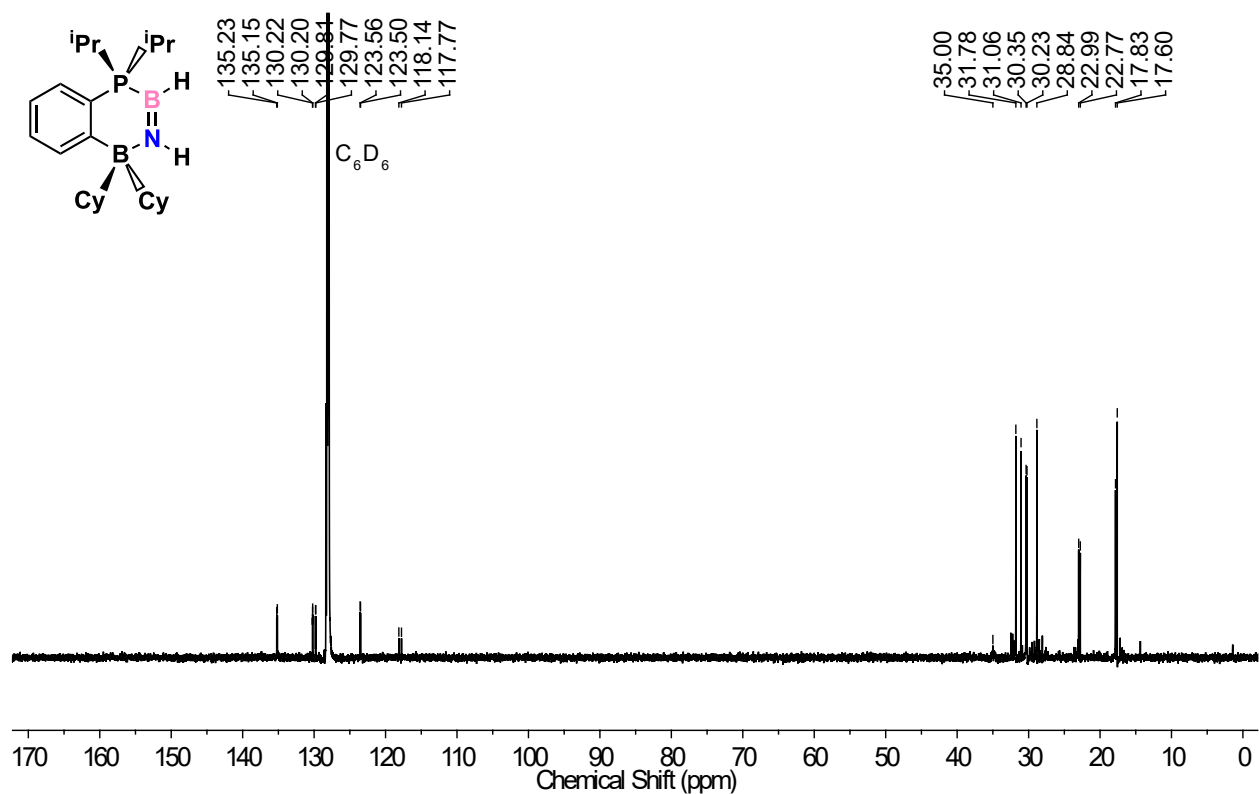


Fig. S21  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{HBNH}\}$  in  $\text{C}_6\text{D}_6$ .

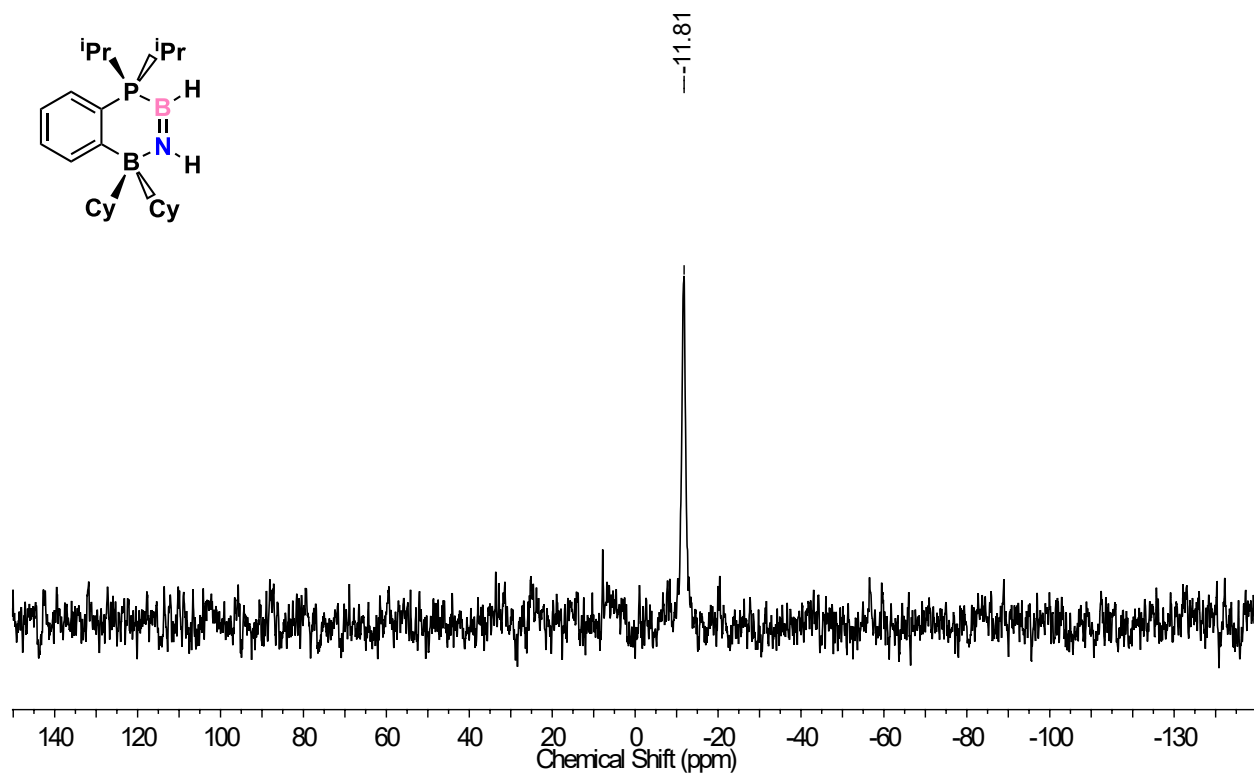


Fig. S22  $^{31}P\{^1H\}$  NMR spectrum of  $PB\{HBNH\}$  in  $C_6D_6$ .

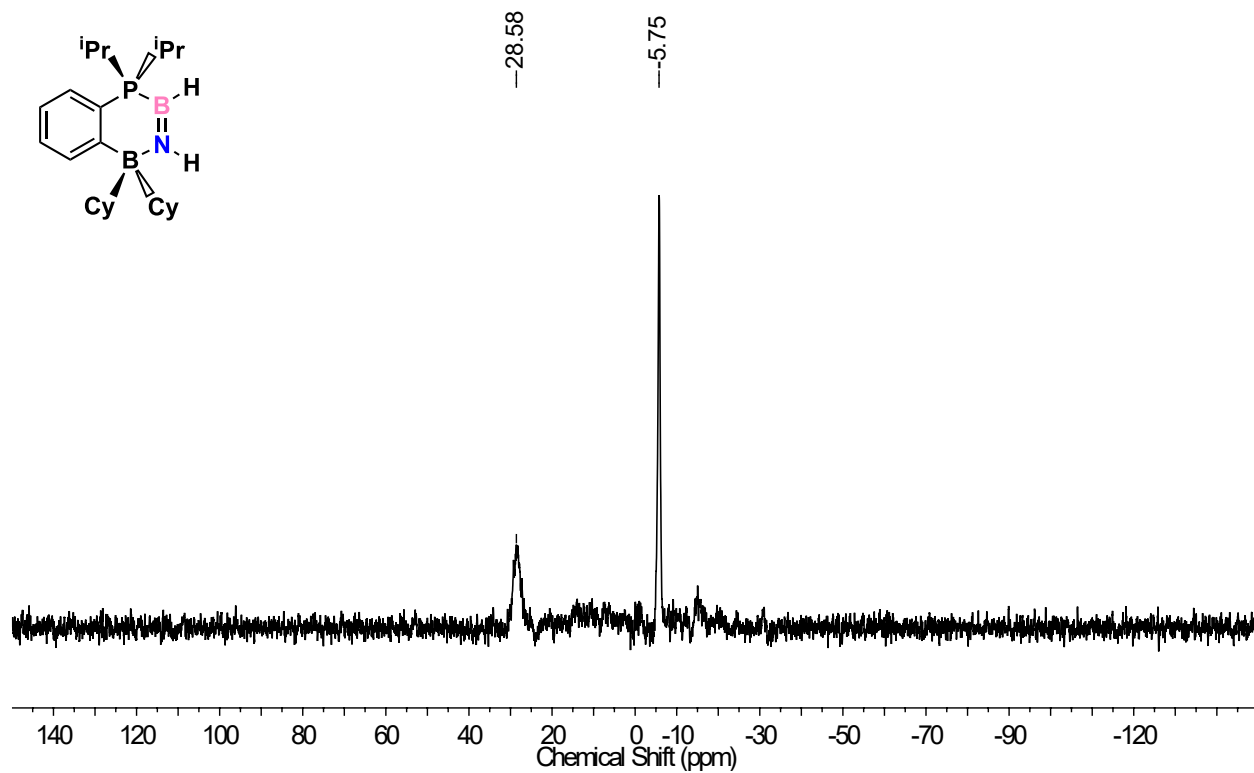
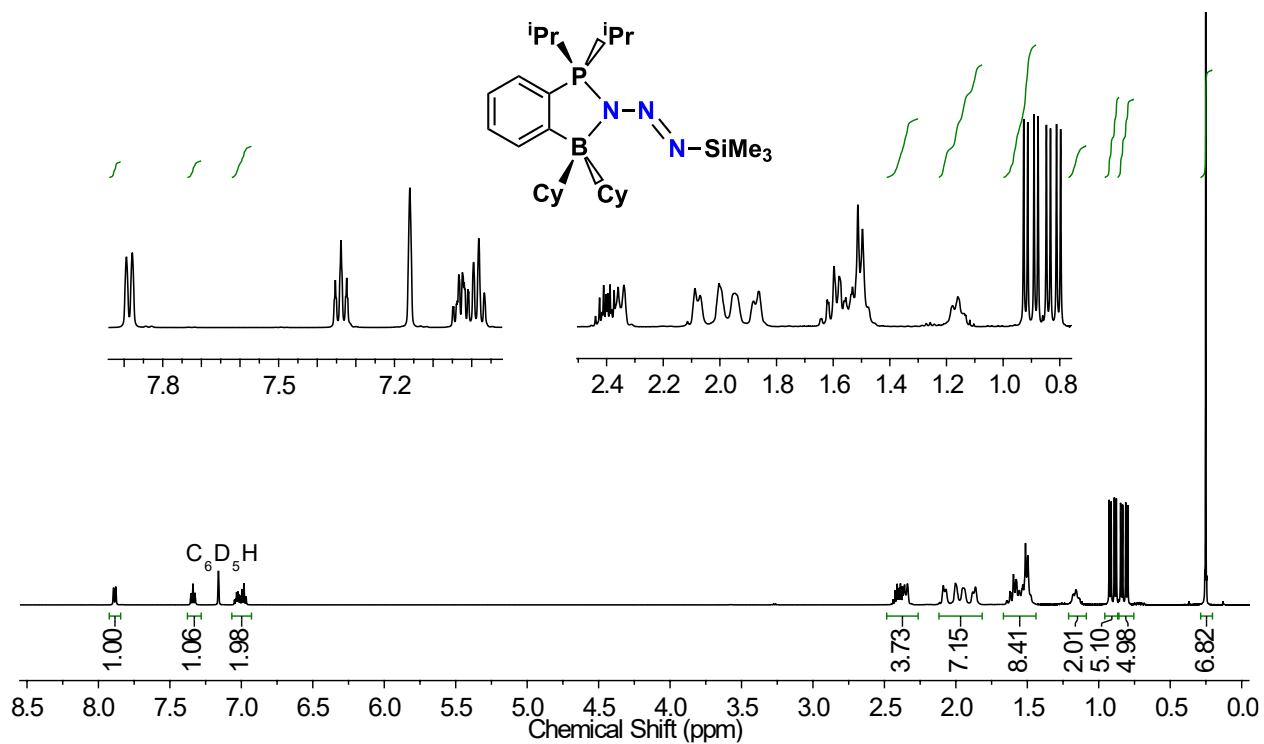
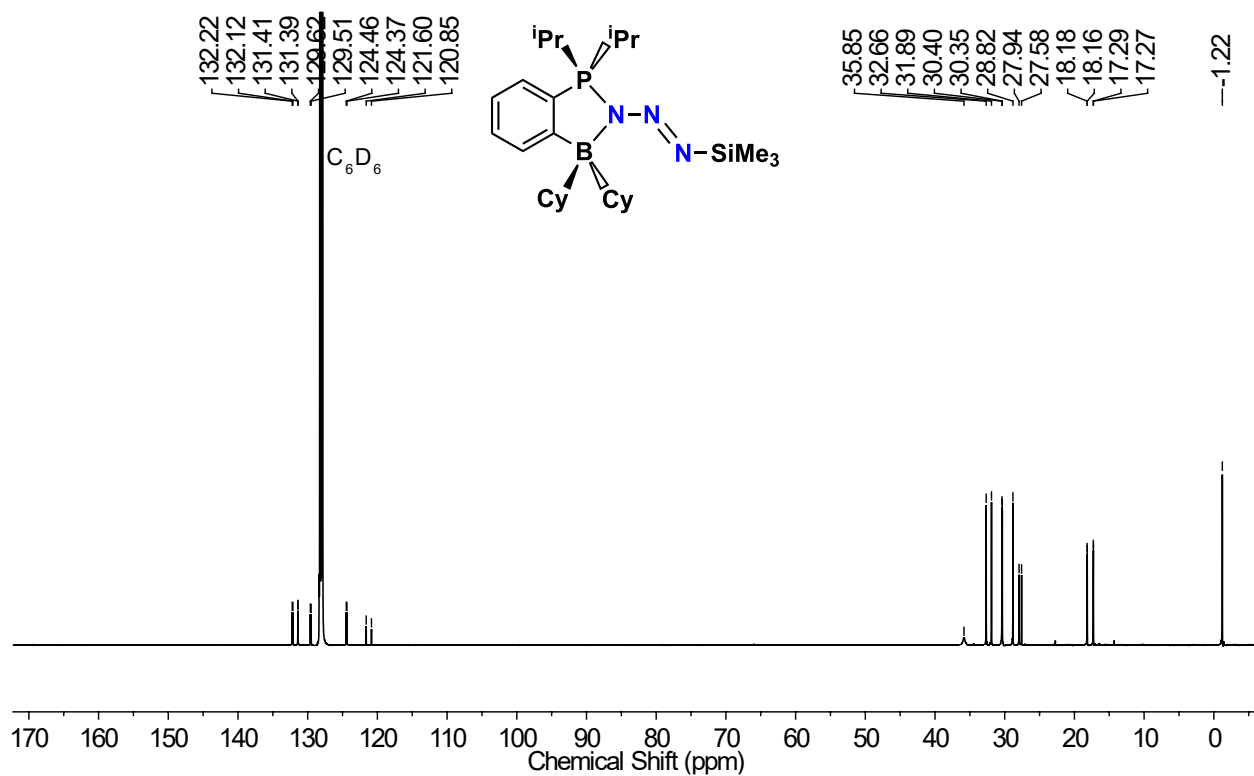


Fig. S23  $^{11}B\{^1H\}$  NMR spectrum of  $PB\{HBNH\}$  in  $C_6D_6$ .



**Fig. S24**  $^1\text{H}$  NMR spectrum of  $\text{PB}\{\text{N}_3\text{SiMe}_3\}$  in  $\text{C}_6\text{D}_6$ .



**Fig. S25**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{N}_3\text{SiMe}_3\}$  in  $\text{C}_6\text{D}_6$ .

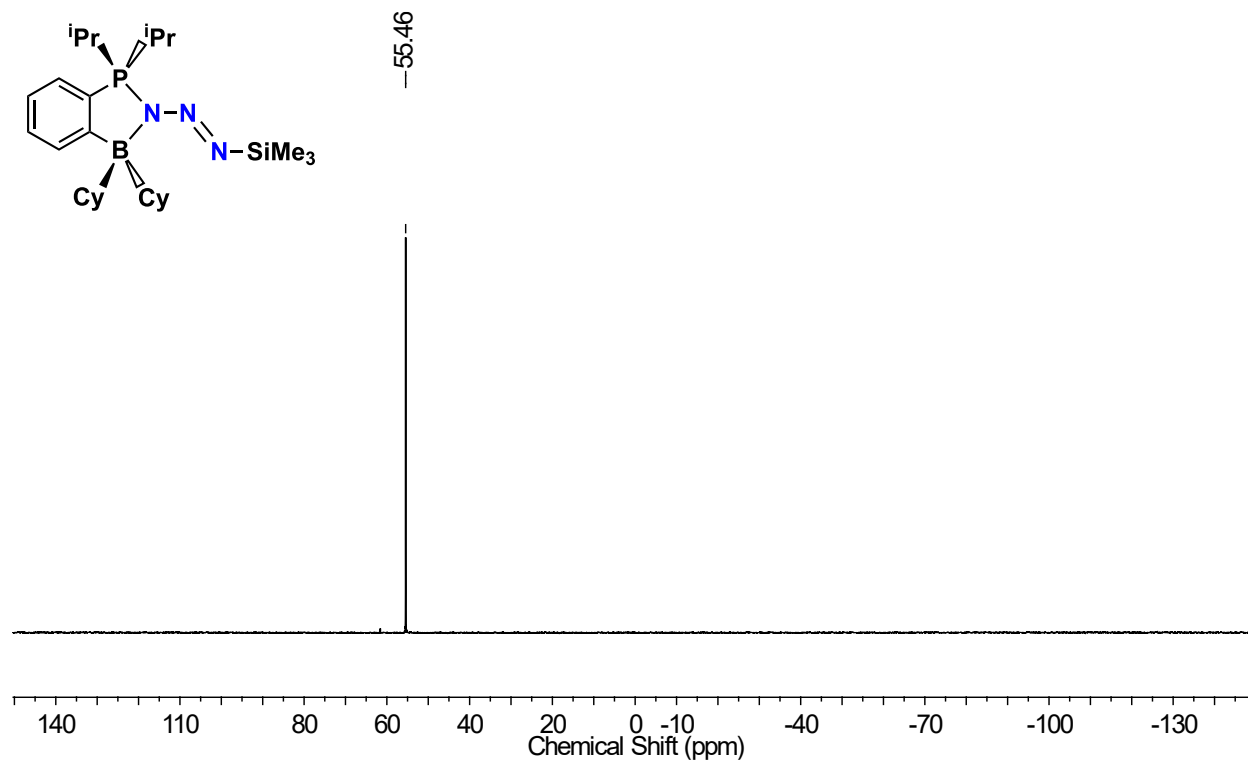


Fig. S26  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{N}_3\text{SiMe}_3\}$  in  $\text{C}_6\text{D}_6$ .

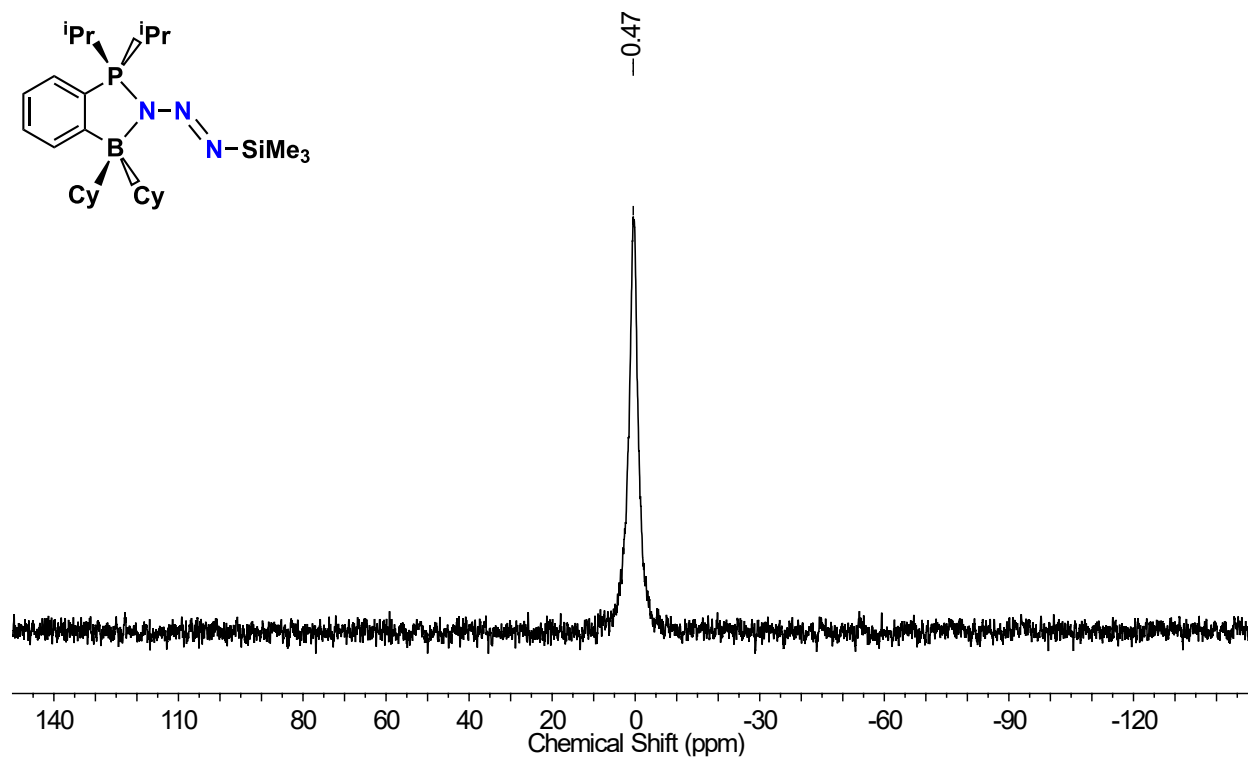


Fig. S27  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{N}_3\text{SiMe}_3\}$  in  $\text{C}_6\text{D}_6$ .

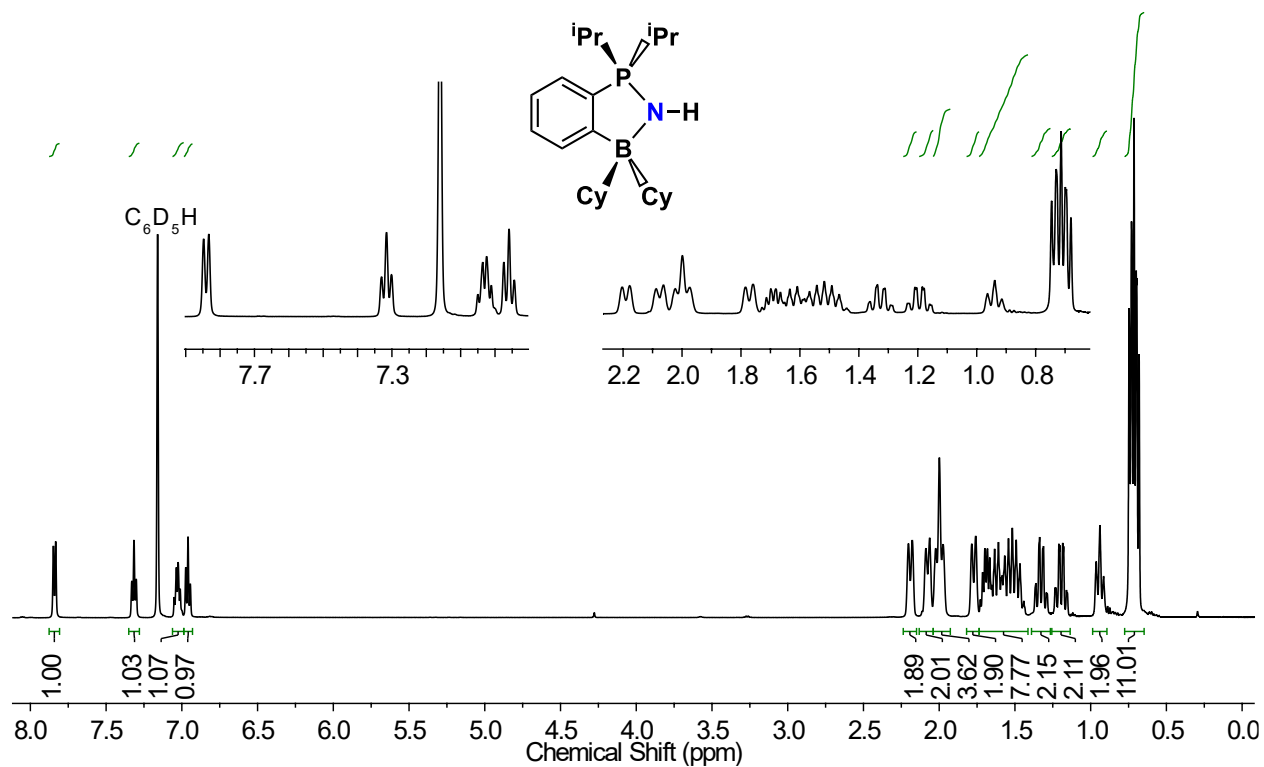


Fig. S28  $^1\text{H}$  NMR spectrum of  $\text{PB}\{\text{NH}\}$  in  $\text{C}_6\text{D}_6$ .

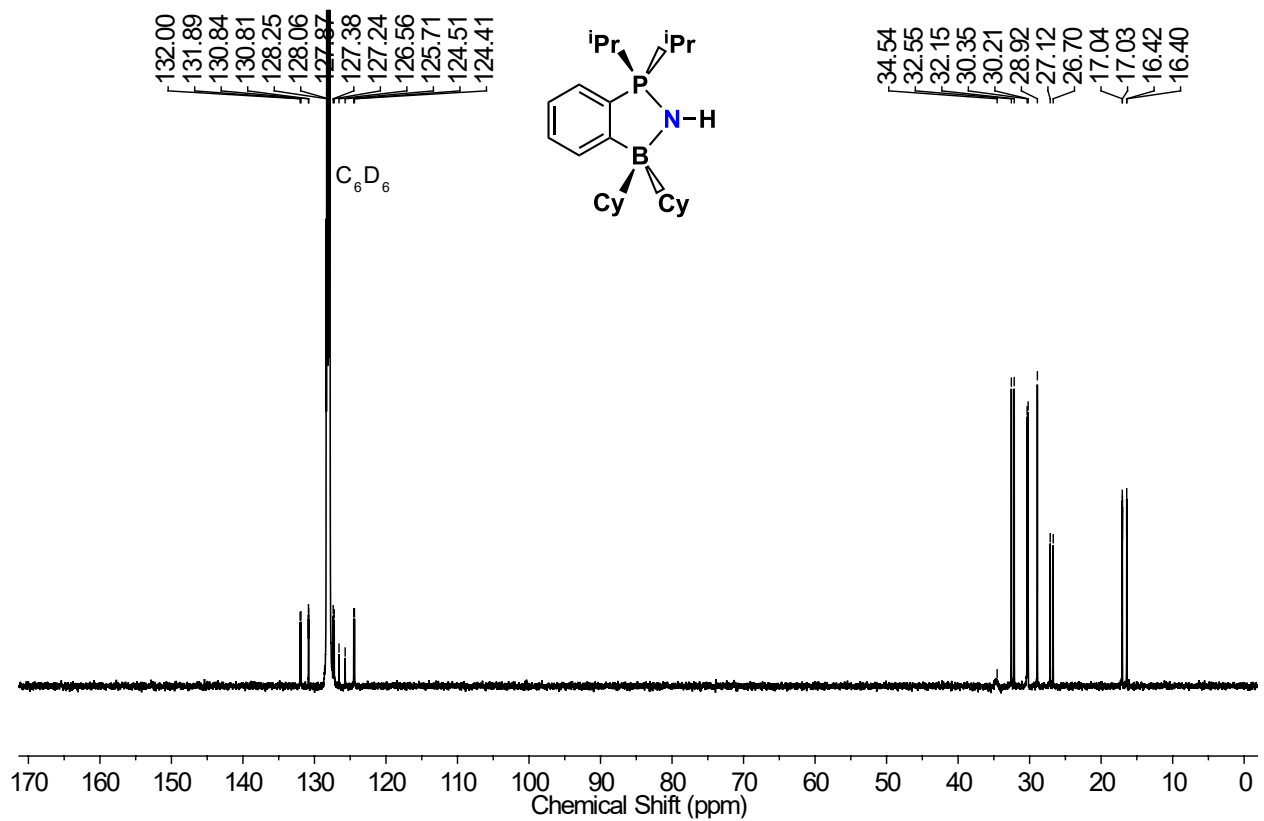
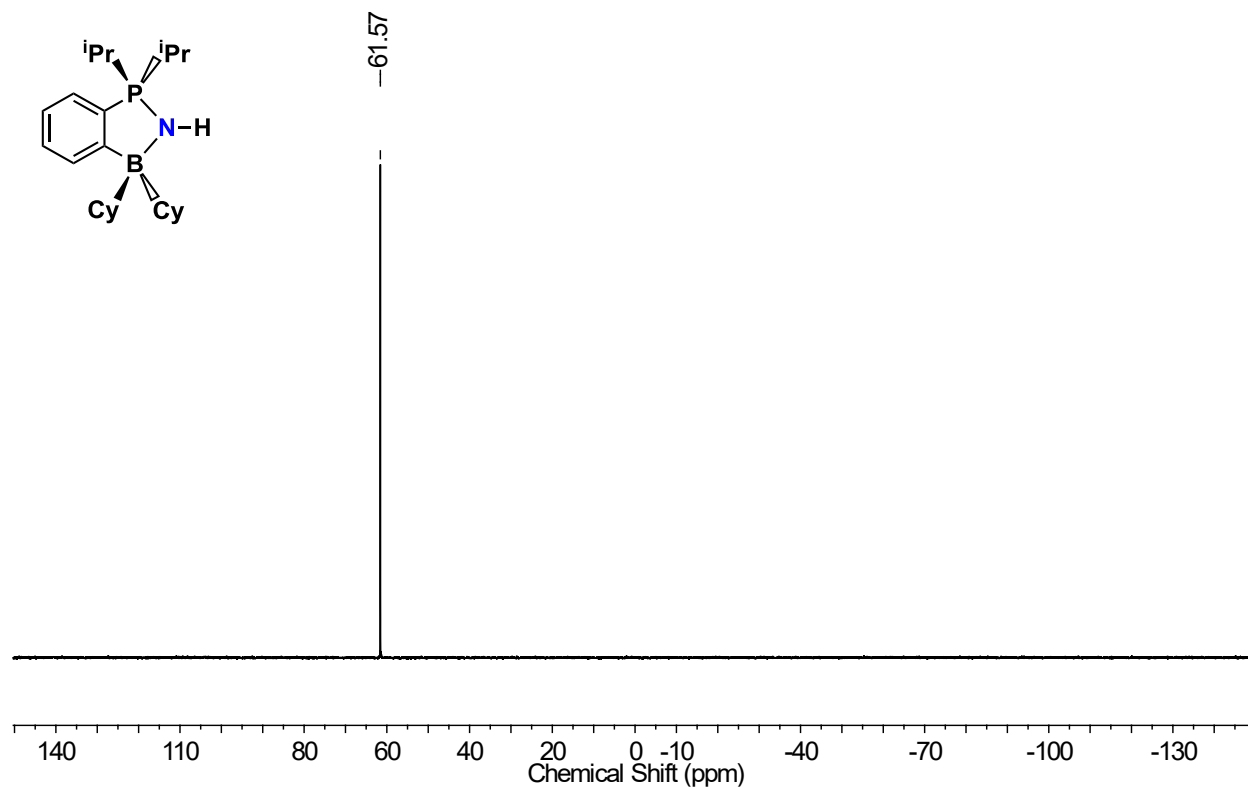
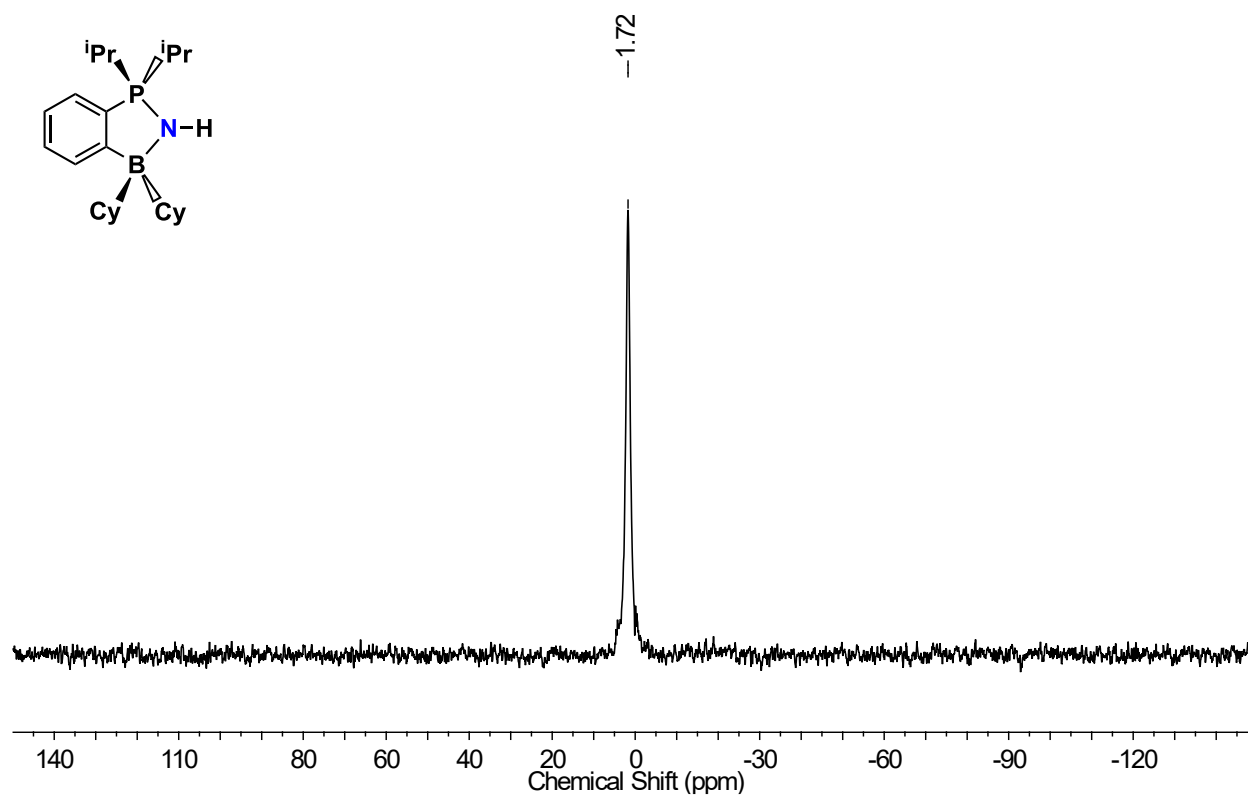


Fig. S29  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{NH}\}$  in  $\text{C}_6\text{D}_6$ .



**Fig. S30**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **PB{NH}** in  $\text{C}_6\text{D}_6$ .



**Fig. S31**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **PB{NH}** in  $\text{C}_6\text{D}_6$ .

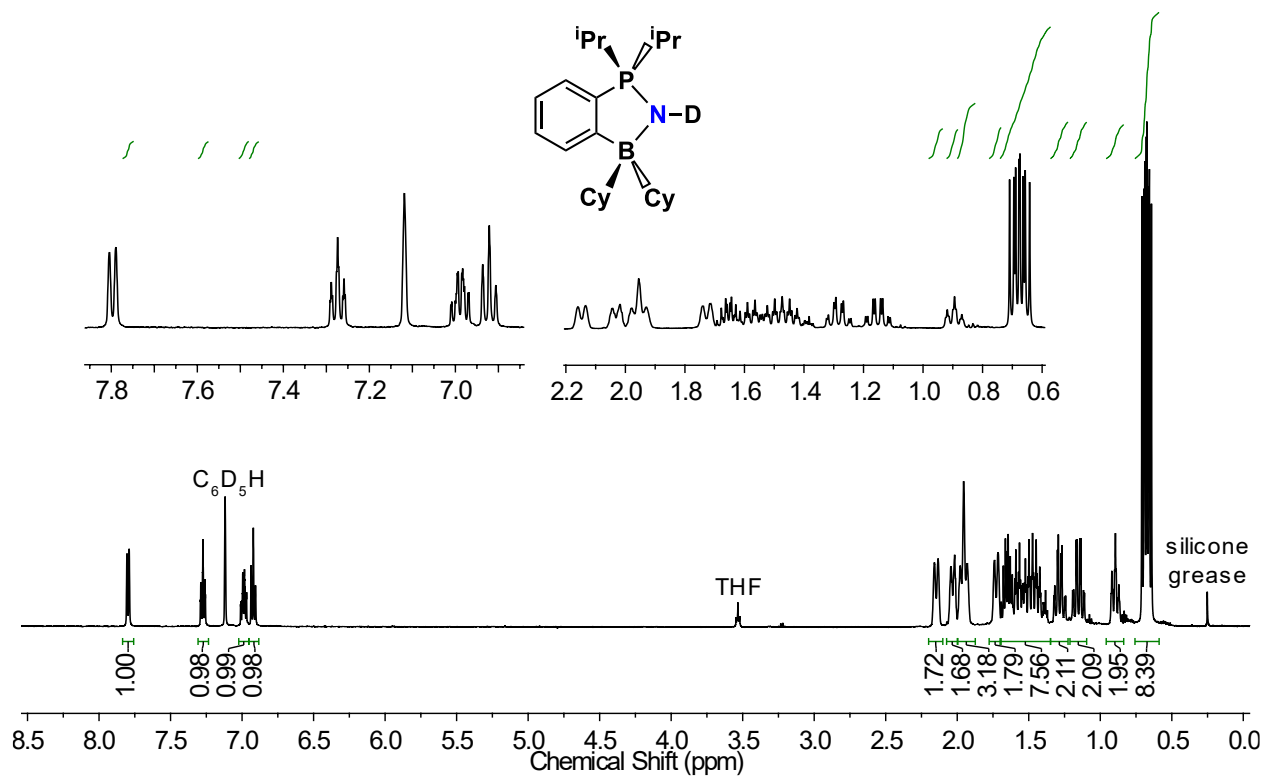


Fig. S32  $^1\text{H}$  NMR spectrum of  $\text{PB}\{\text{ND}\}$  in  $\text{C}_6\text{D}_6$ .

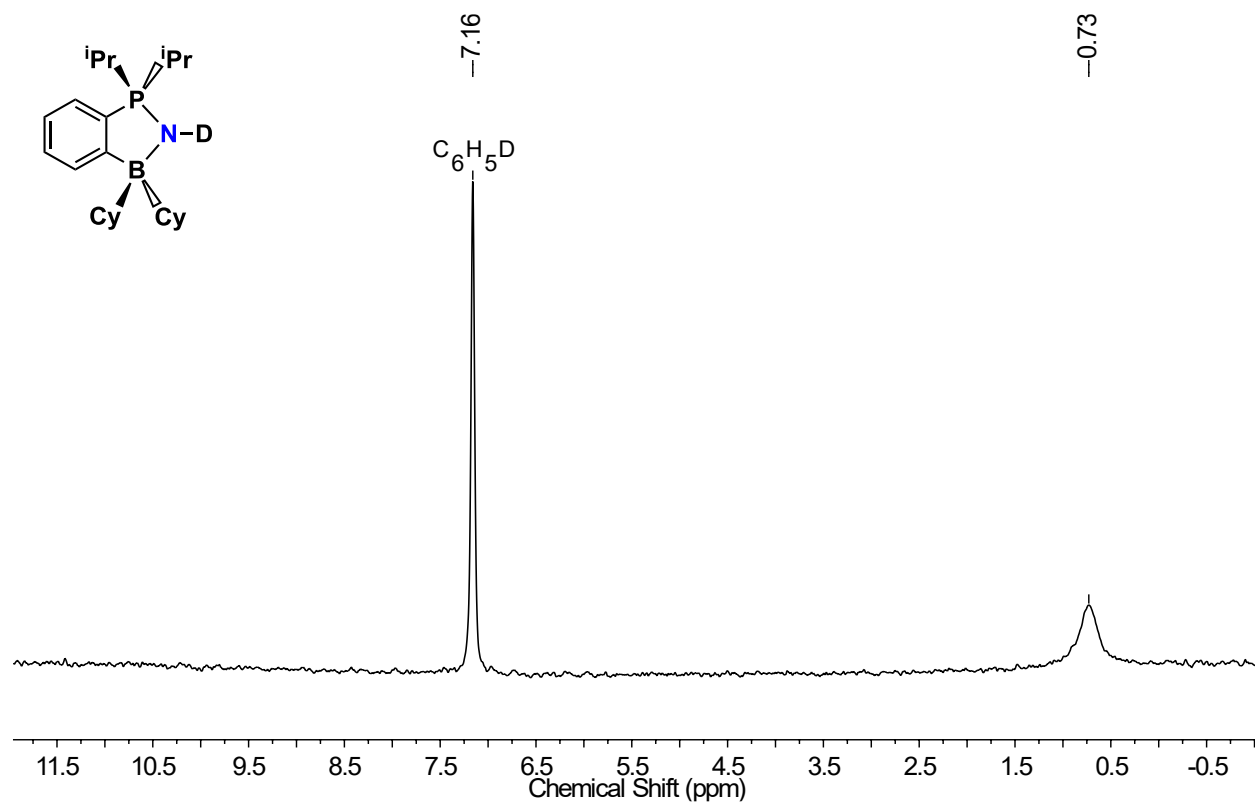


Fig. S33  $^2\text{H}$  NMR spectrum of  $\text{PB}\{\text{ND}\}$  in  $\text{C}_6\text{H}_6$ .



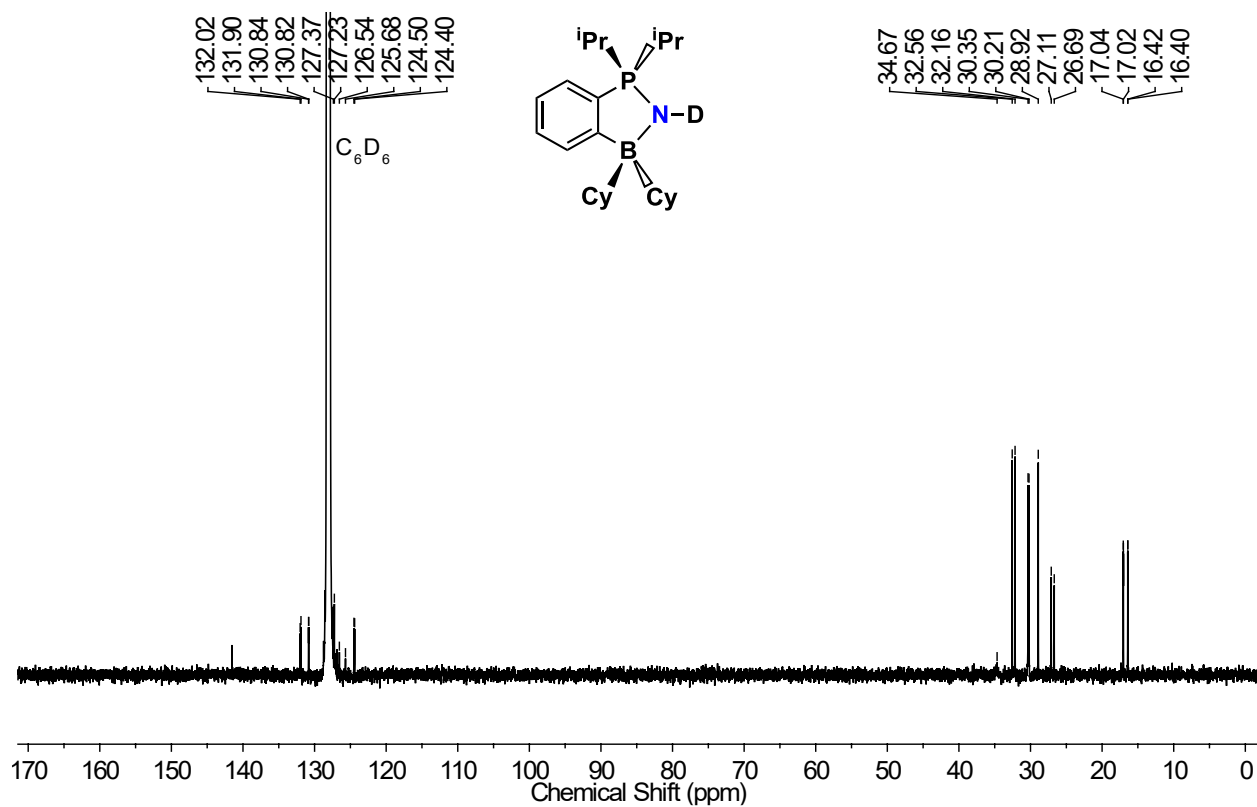


Fig. S34  $^{13}C\{^1H\}$  NMR spectrum of **PB{ND}** in  $C_6D_6$ .

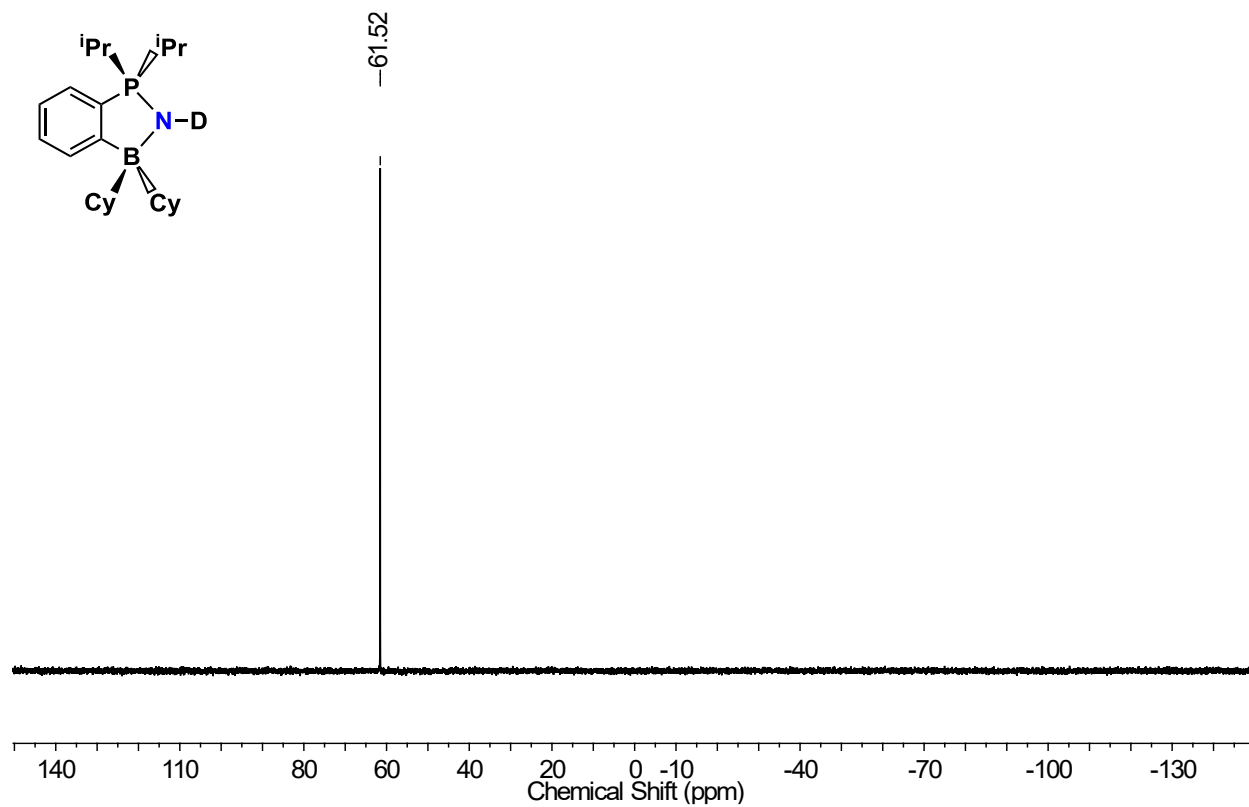


Fig. S35  $^{31}P\{^1H\}$  NMR spectrum of **PB{ND}** in  $C_6D_6$ .

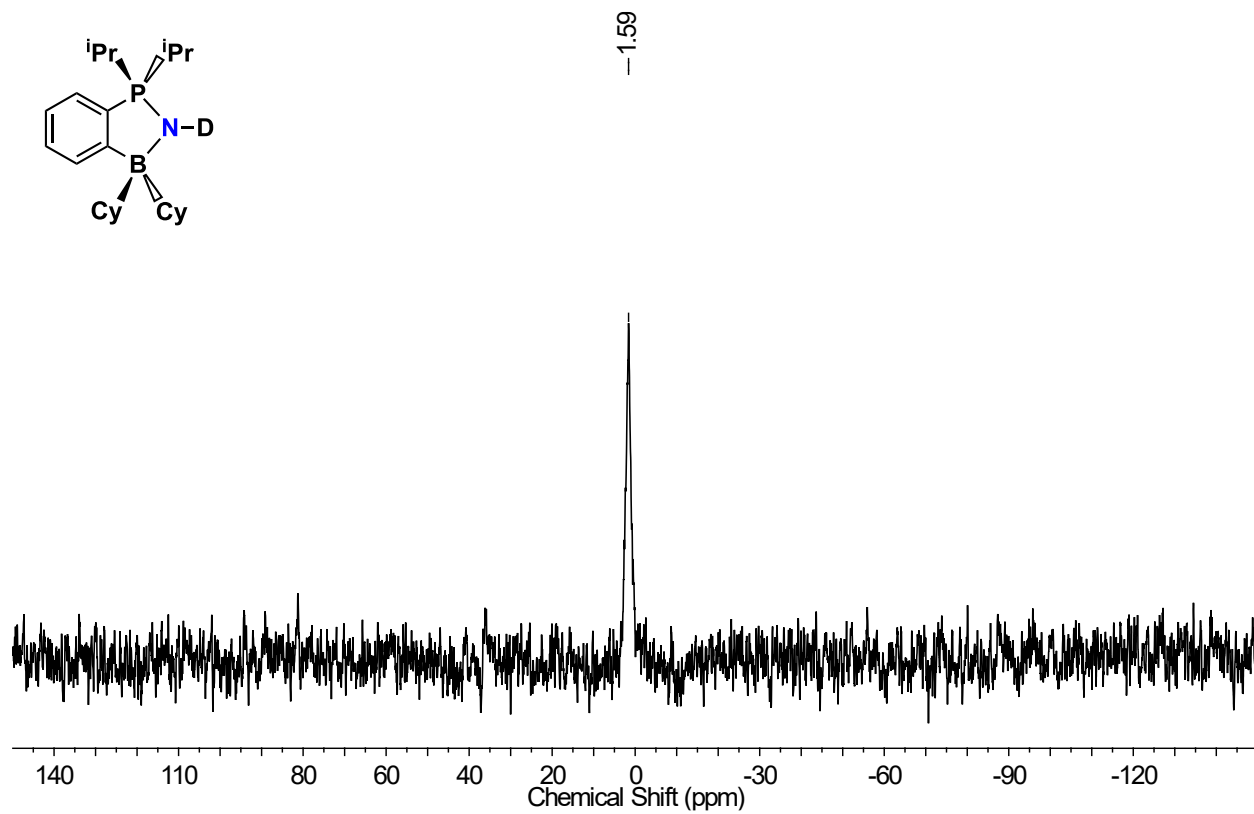


Fig. S36  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{ND}\}$  in  $\text{C}_6\text{D}_6$ .

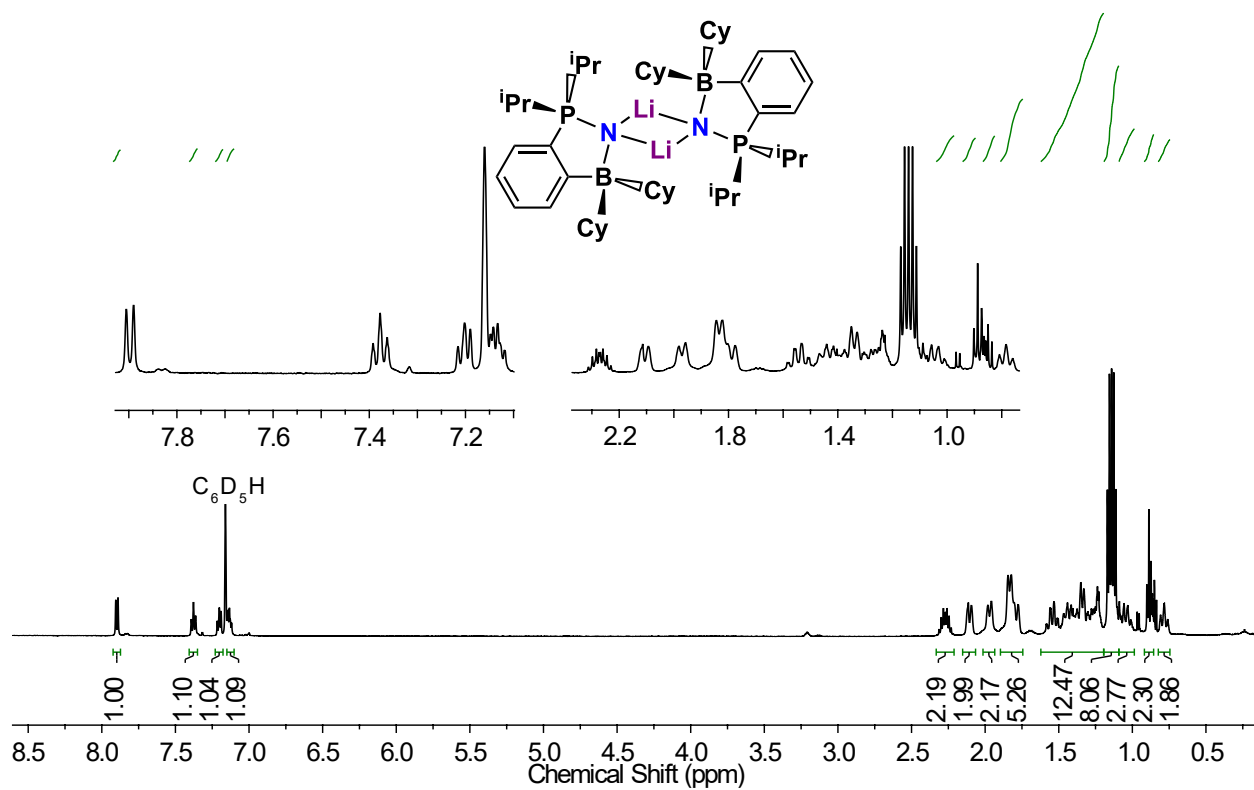


Fig. S37  $^1\text{H}$  NMR spectrum of  $[\text{PB}\{\text{NLi}\}]_2$  in  $\text{C}_6\text{D}_6$ .

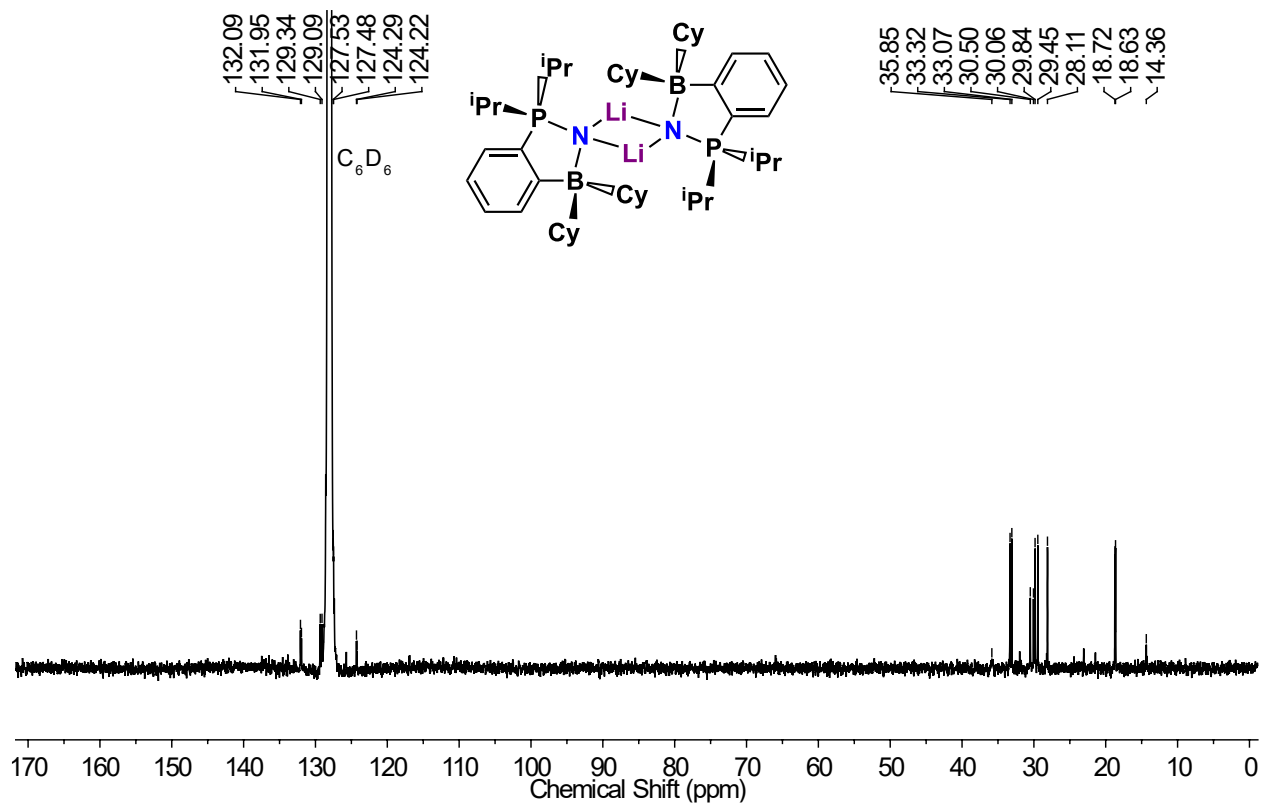


Fig. S38  $^{13}C\{^1H\}$  NMR spectrum of  $[PB\{NLi\}]_2$  in  $C_6D_6$ .

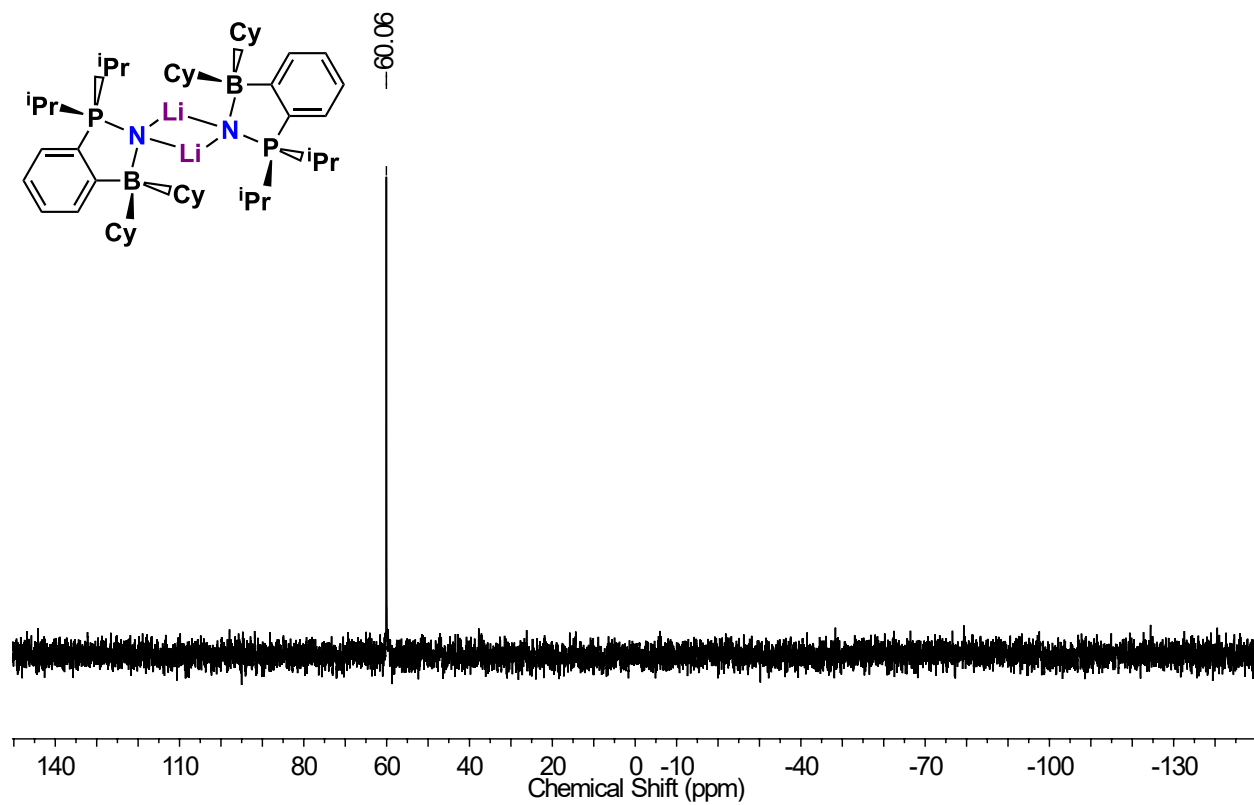


Fig. S39  $^{31}P\{^1H\}$  NMR spectrum of  $[PB\{NLi\}]_2$  in  $C_6D_6$ .

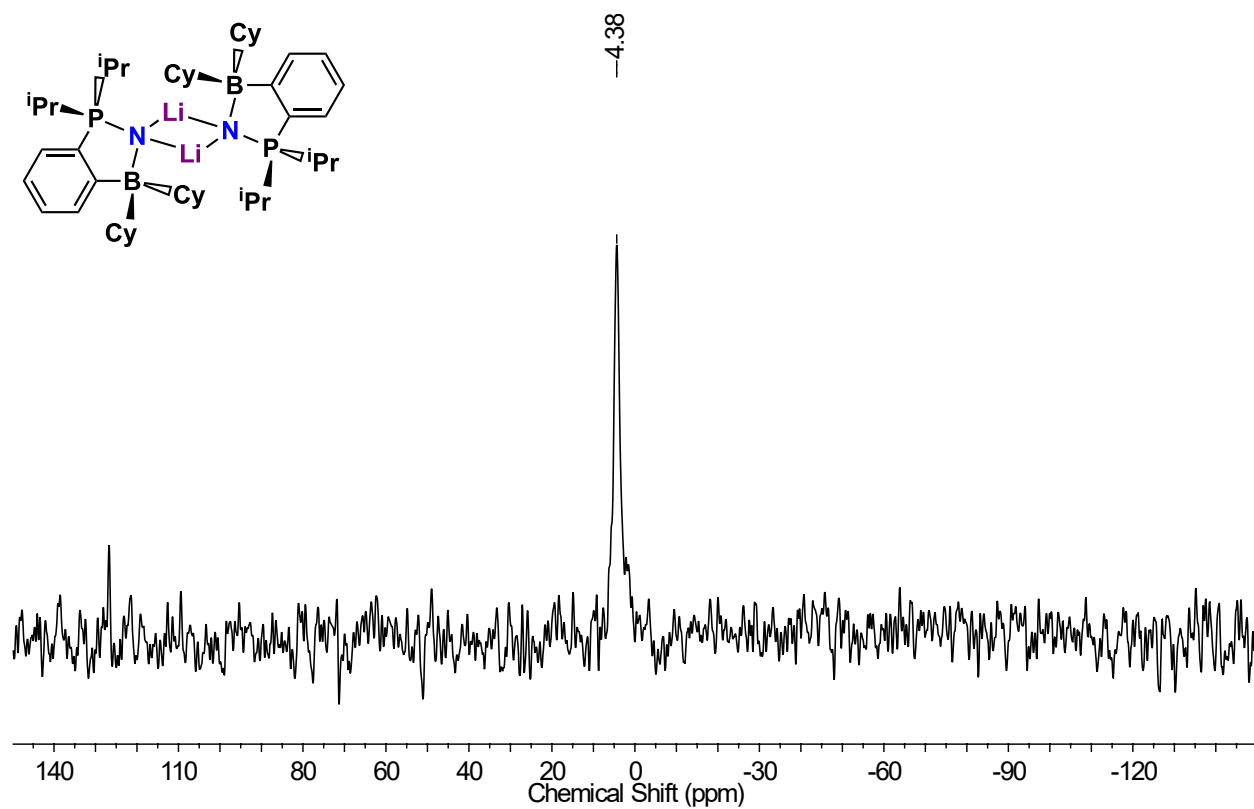


Fig. S40  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{PB}\{\text{NLi}\}]_2$  in  $\text{C}_6\text{D}_6$ .

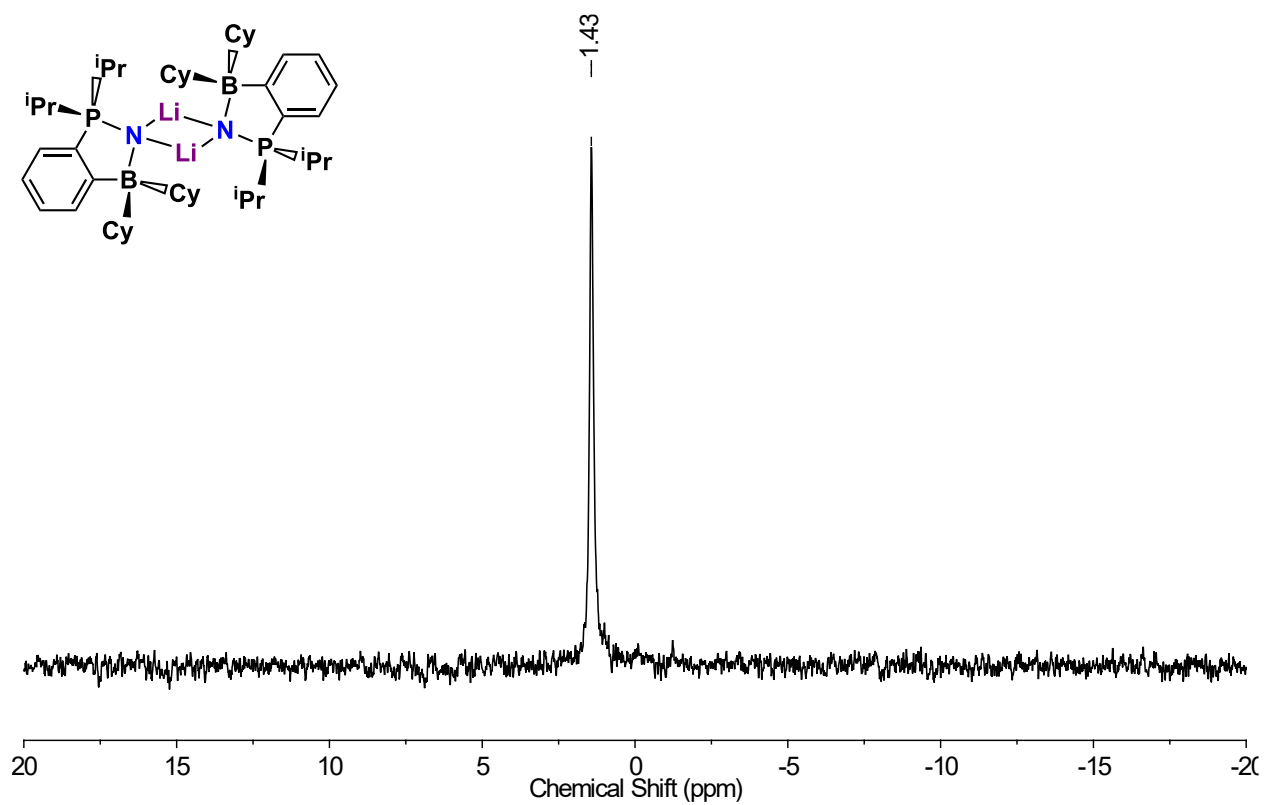


Fig. S41  $^7\text{Li}\{^1\text{H}\}$  NMR spectrum of  $[\text{PB}\{\text{NLi}\}]_2$  in  $\text{C}_6\text{D}_6$ .

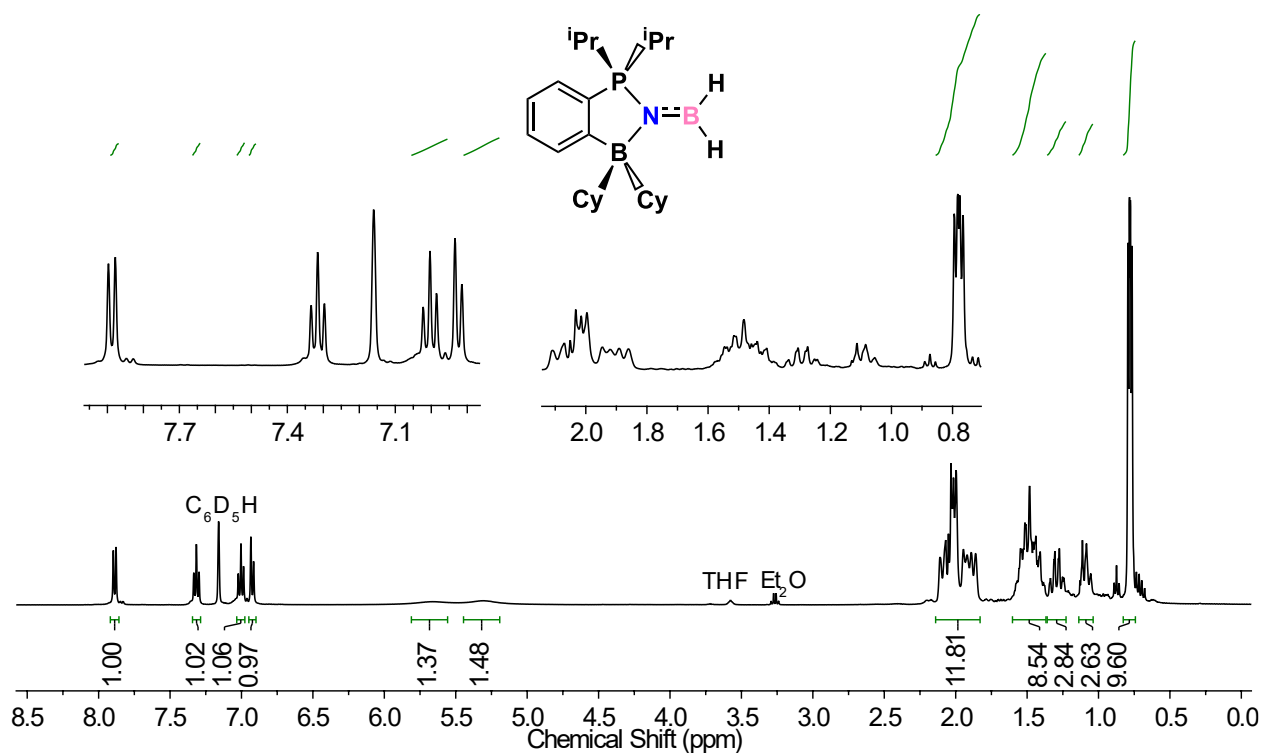


Fig. S42  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum of  $\text{PB}\{\text{NBH}_2\}$  in  $\text{C}_6\text{D}_6$ .

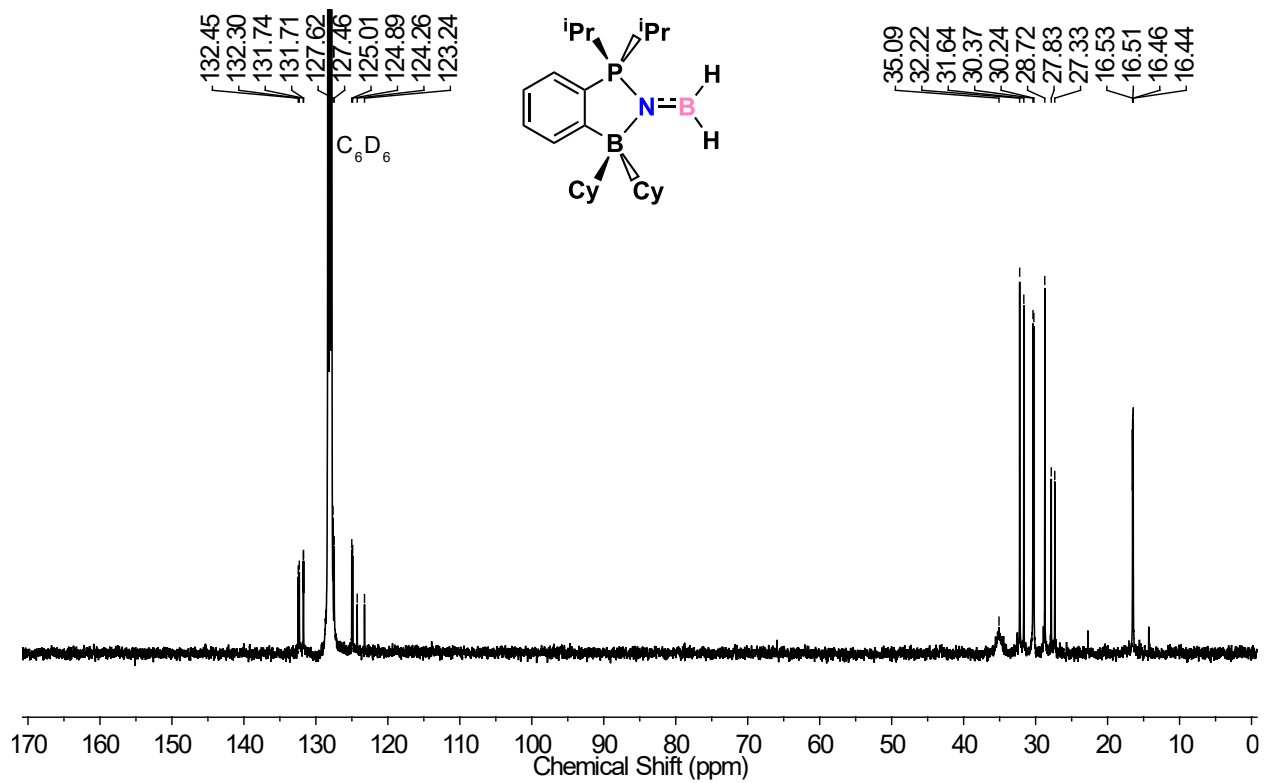


Fig. S43  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{NBH}_2\}$  in  $\text{C}_6\text{D}_6$ .

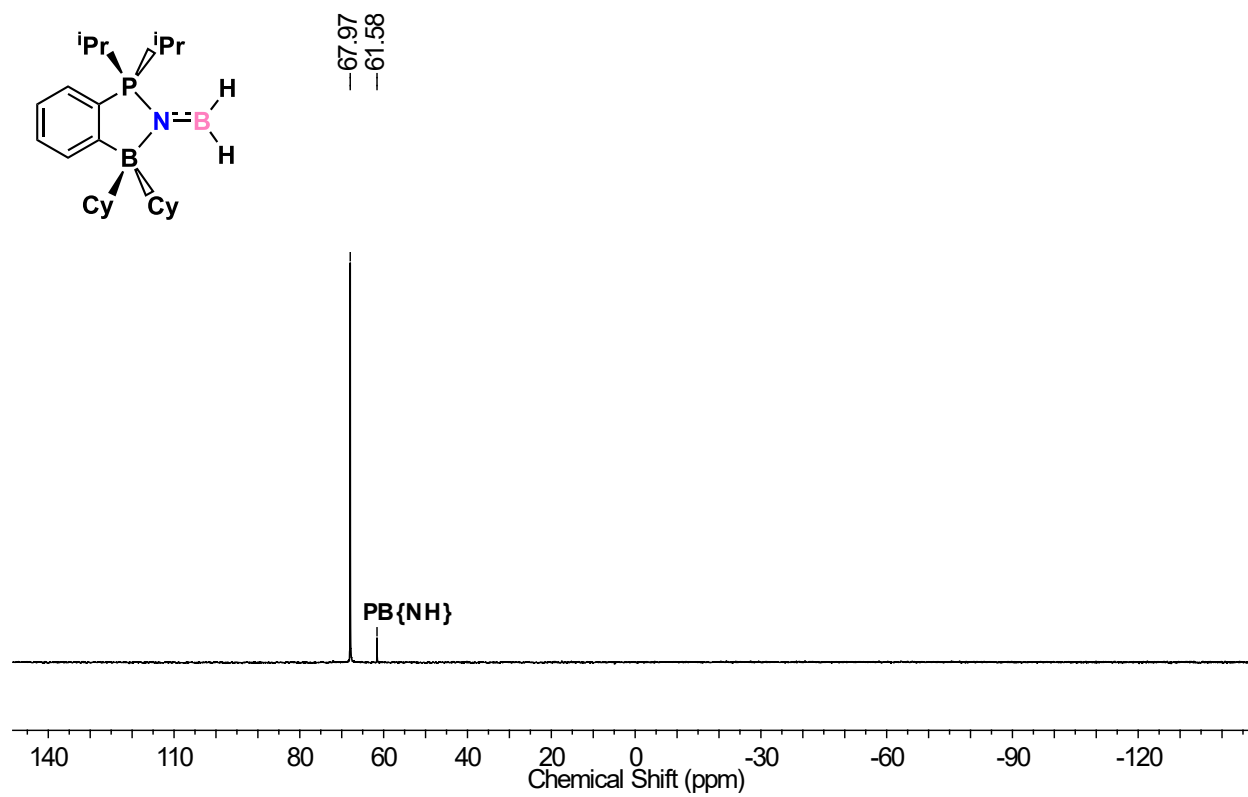


Fig. S44  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{NBH}_2\}$  in  $\text{C}_6\text{D}_6$ .

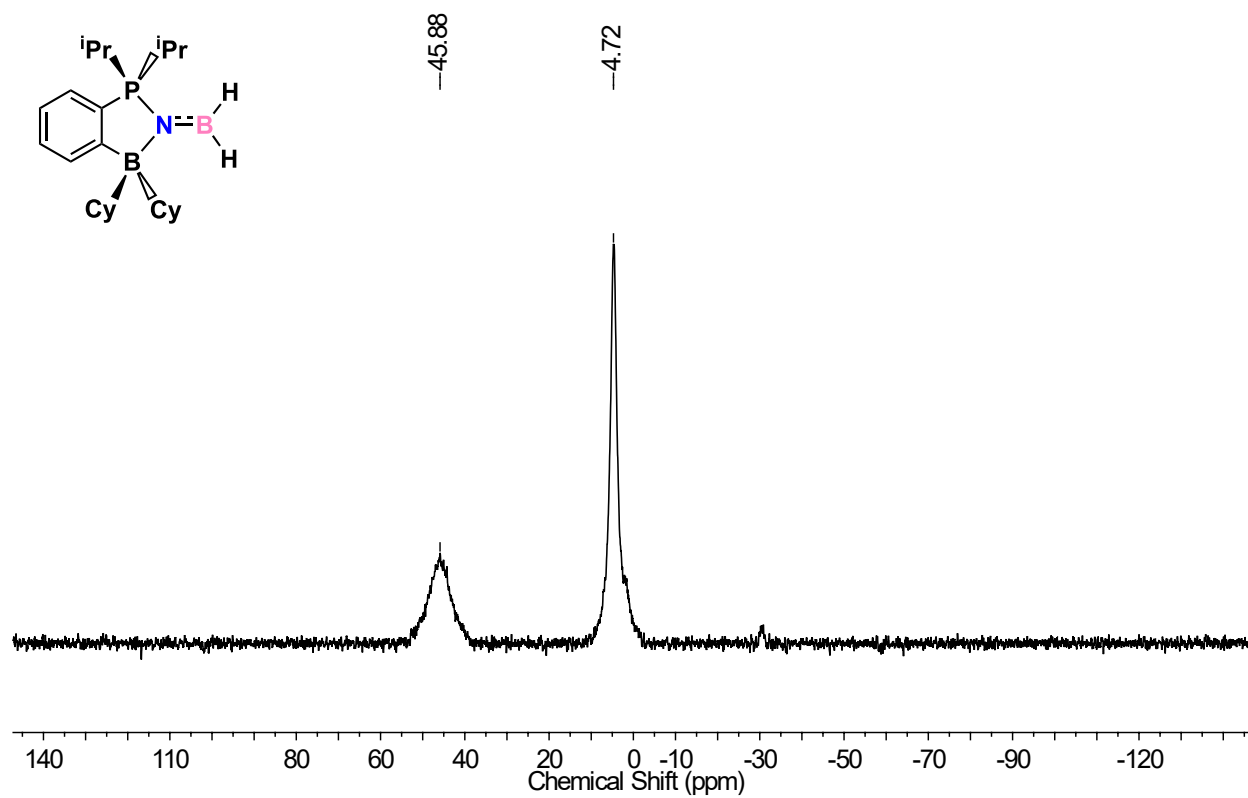


Fig. S45  $^{11}\text{B}$  NMR spectrum of  $\text{PB}\{\text{NBH}_2\}$  in  $\text{C}_6\text{D}_6$ .

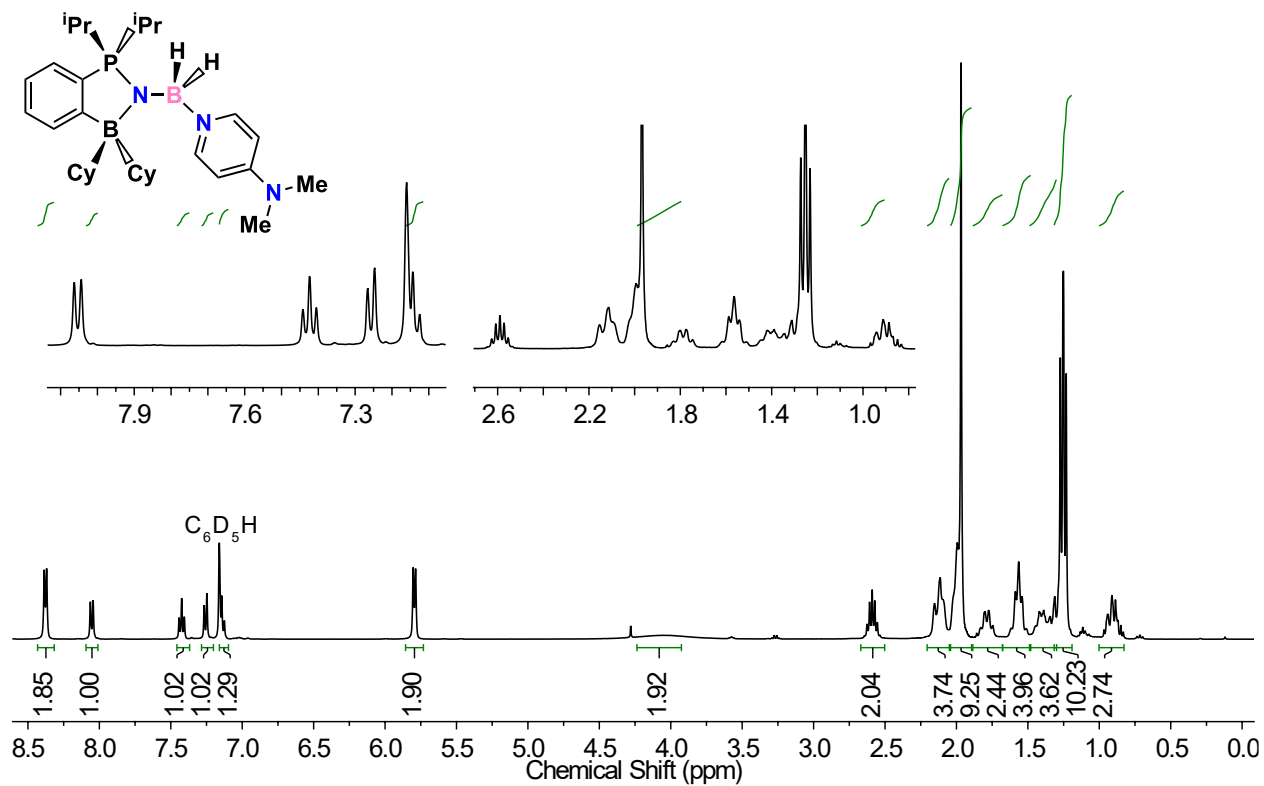


Fig. S46  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum of  $\text{PB}\{\text{NBH}_2\}\cdot\text{DMAP}$  in  $\text{C}_6\text{D}_6$ .

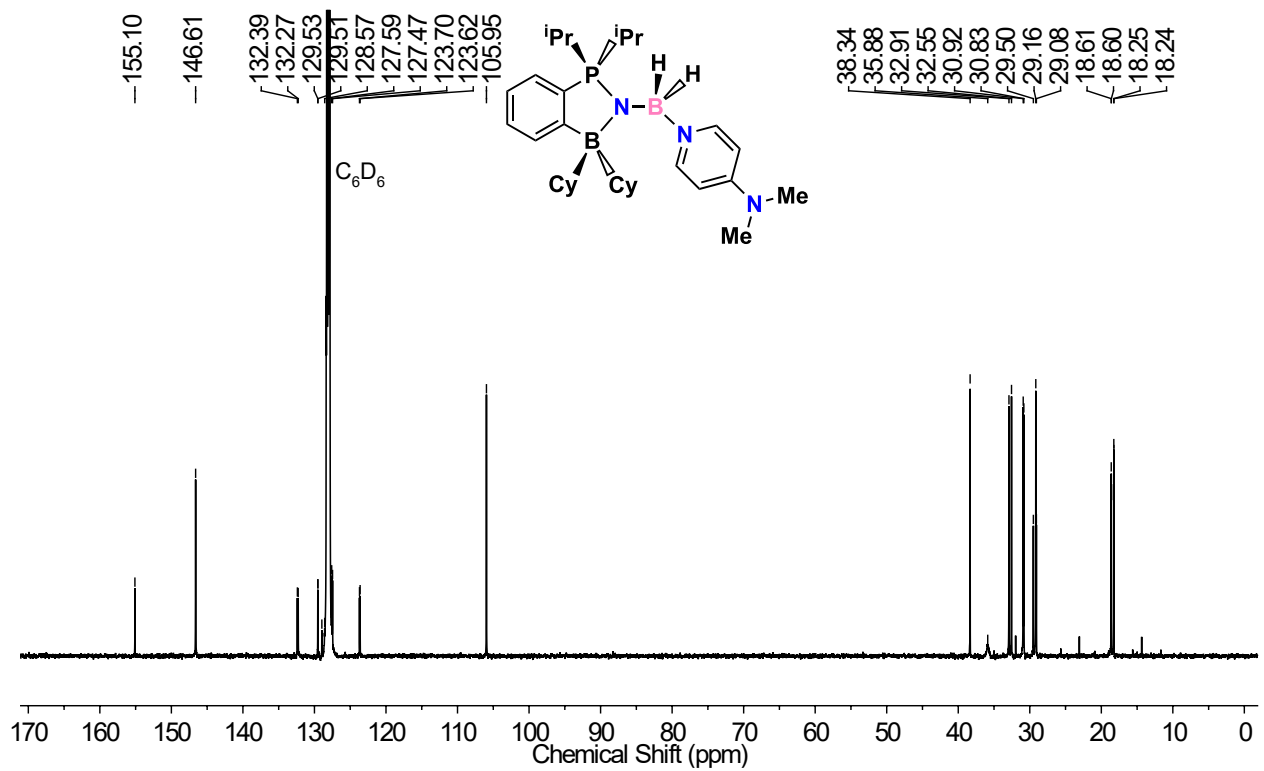
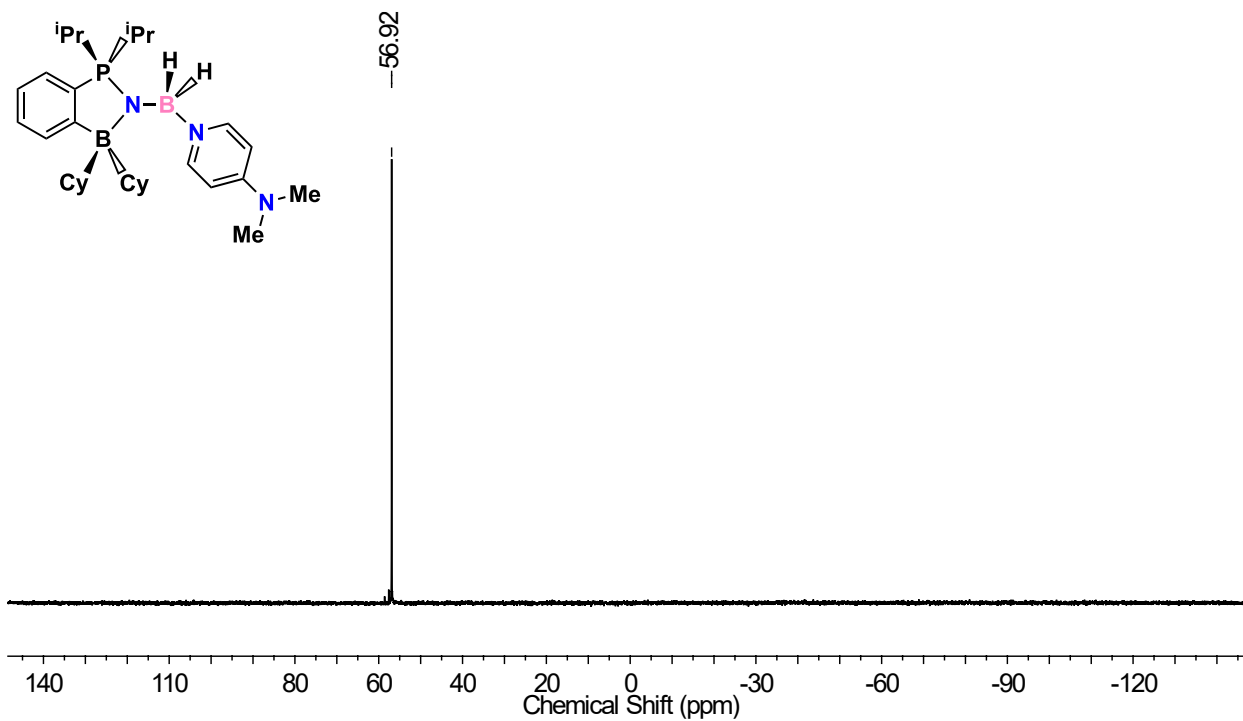
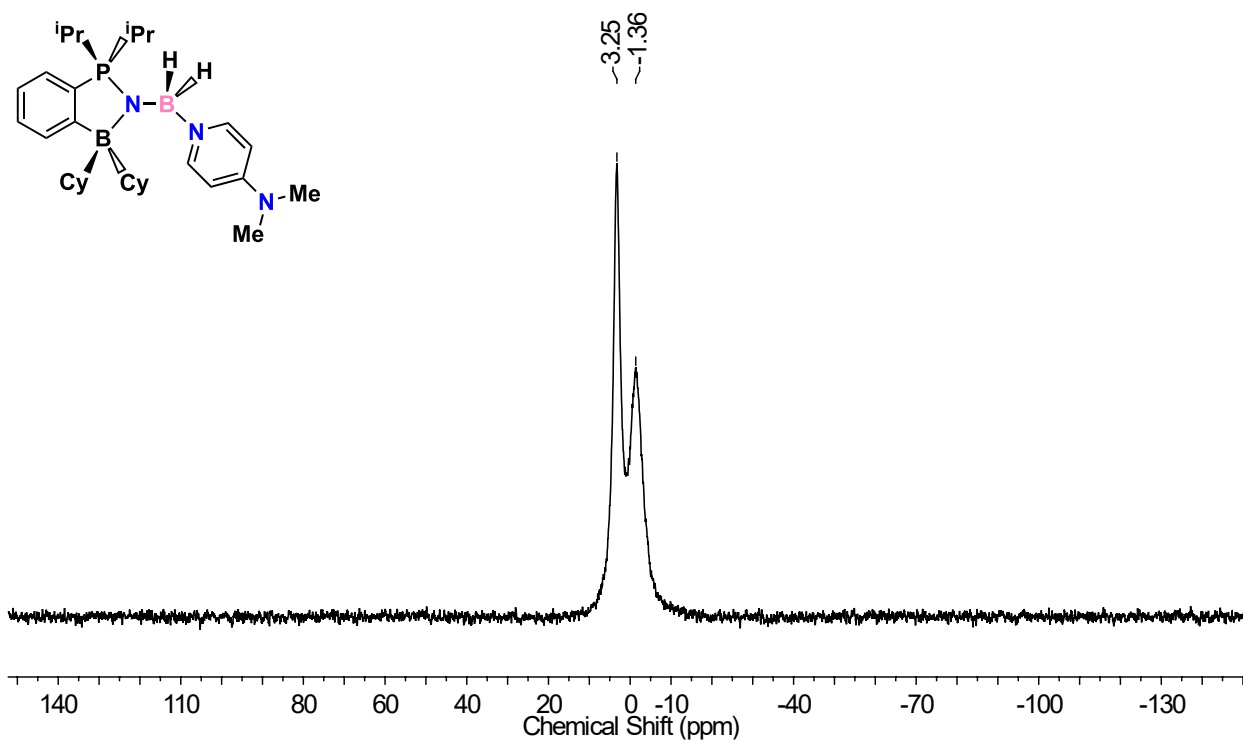


Fig. S47  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{NBH}_2\}\cdot\text{DMAP}$  in  $\text{C}_6\text{D}_6$ .



**Fig. S48**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{PB}\{\text{NBH}_2\}\cdot\text{DMAP}$  in  $\text{C}_6\text{D}_6$ .



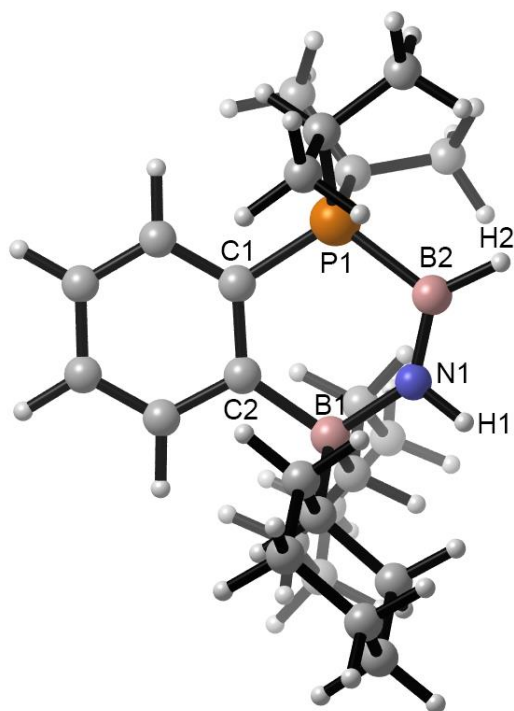
**Fig. S49**  $^{11}\text{B}$  NMR spectrum of  $\text{PB}\{\text{NBH}_2\}\cdot\text{DMAP}$  in  $\text{C}_6\text{D}_6$ .



## 5. Density Functional Theory (DFT) Computations

Structure geometries were optimized in the gas phase using the M06-2X<sup>S8</sup> functional and the cc-pVTZ<sup>S9</sup> basis set using Gaussian16.<sup>S10</sup> Frequency analyses were performed to confirm the presence of no imaginary frequencies (for ground states), or one imaginary frequency (for transition states). Optimized geometries were visualized with CYLview,<sup>S11</sup> and orbitals were rendered using VMD.<sup>S12</sup> NBO analysis was performed at the M06-2X/cc-pVTZ level of theory using the NBO 6.0 program.<sup>S13</sup> The barrier of rotation about the exocyclic B–N bond in **PB{NBH<sub>2</sub>}** was computed by optimizing the geometry with various fixed P–N–B–H dihedral angles, as well as optimizing the transition state for the bond rotation. The rotation barrier was then calculated as the free energy difference between the ground state and transition state geometries. IR frequencies were corrected by a scaling factor of 0.946.<sup>S14</sup>

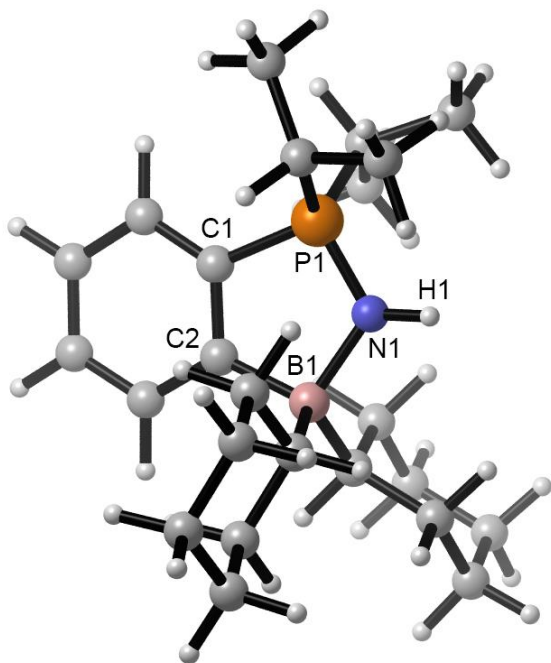
**Table S4** Optimized gas phase geometry of **PB{HBNH}** with (a) calculated and experimental bond lengths [Å], and (b) Wiberg bond indices (WBI) and natural charges ( $Q_{\text{NPA}}$ ) for **PB{HBNH}**.



(a)	Bond	Calculated	Experimental
	C1–P1	1.797	1.7945(18)
	P1–B2	1.935	1.927(2)
	B2–N1	1.356	1.347(3)
	B1–N1	1.575	1.579(3)
	C2–B1	1.641	1.645(3)

(b)	Bond	WBI	Atom	$Q_{\text{NPA}}$
	C1–P1	0.95	P1	1.26
	P1–B2	0.92	B2	0.26
	B2–N1	1.43	H2	-0.04
	B1–N1	0.69	N1	-0.97
	C2–B1	0.83	H1	0.40
	-	-	B1	0.61

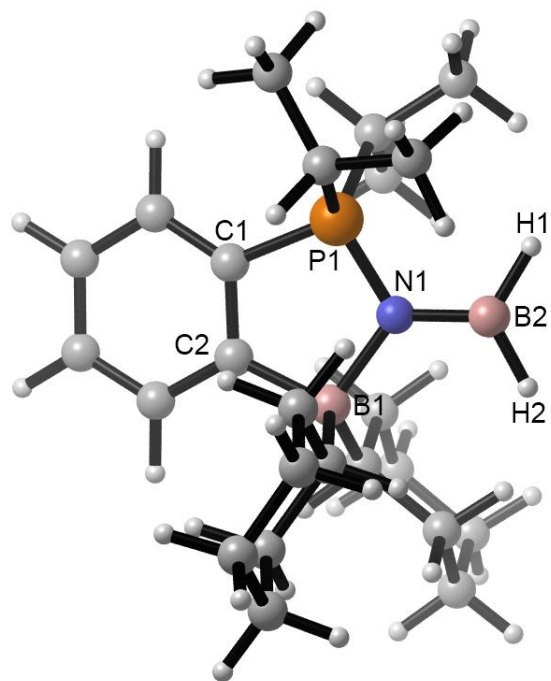
**Table S5** Optimized gas phase geometry of **PB{NH}** with (a) calculated and experimental bond lengths [Å], and (b) Wiberg bond indices (WBI) and natural charges ( $Q_{\text{NPA}}$ ) for **PB{NH}**.



(a)	Bond	Calculated	Experimental
	C1–P1	1.785	1.7839(12)
	P1–N1	1.617	1.6092(10)
	B1–N1	1.627	1.6223(15)
	C2–B1	1.629	1.6318(16)

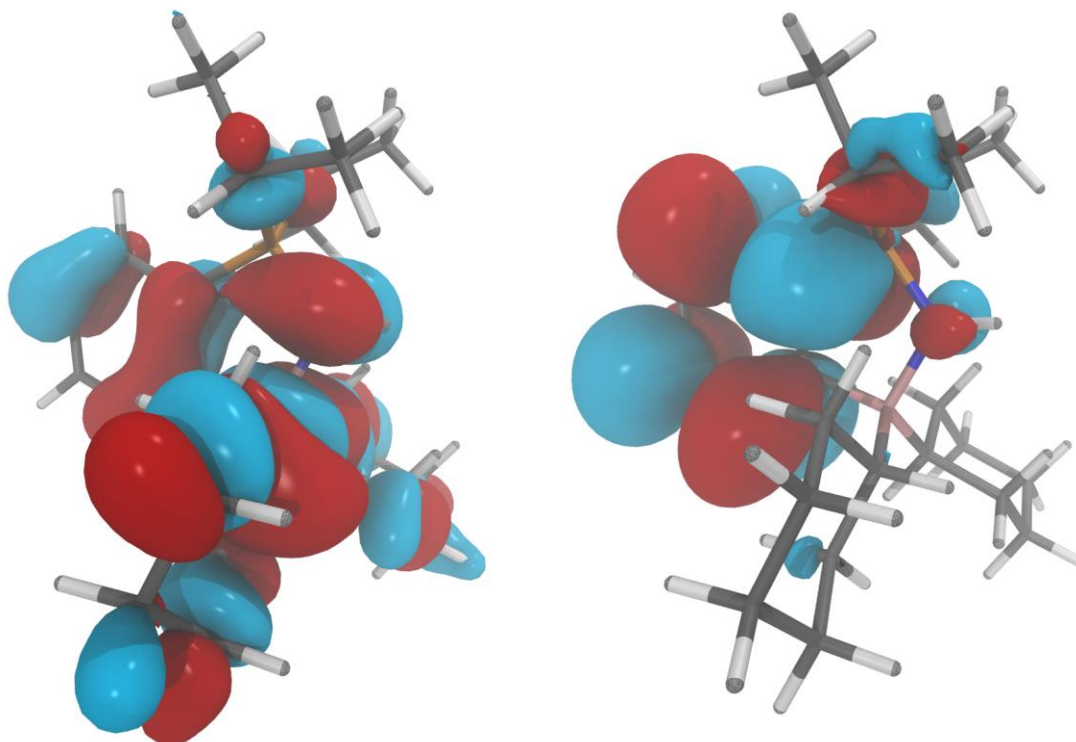
(b)	Bond	WBI	Atom	$Q_{\text{NPA}}$
	C1–P1	0.92	P1	1.86
	P1–N1	1.00	N1	-1.23
	B1–N1	0.65	H1	0.41
	C2–B1	0.83	B1	0.64

**Table S6** Optimized gas phase geometry of **PB{NBH<sub>2</sub>}** with (a) calculated and experimental bond lengths [Å], and (b) Wiberg bond indices (WBI) and natural charges ( $Q_{\text{NPA}}$ ) for **PB{NBH<sub>2</sub>}**.

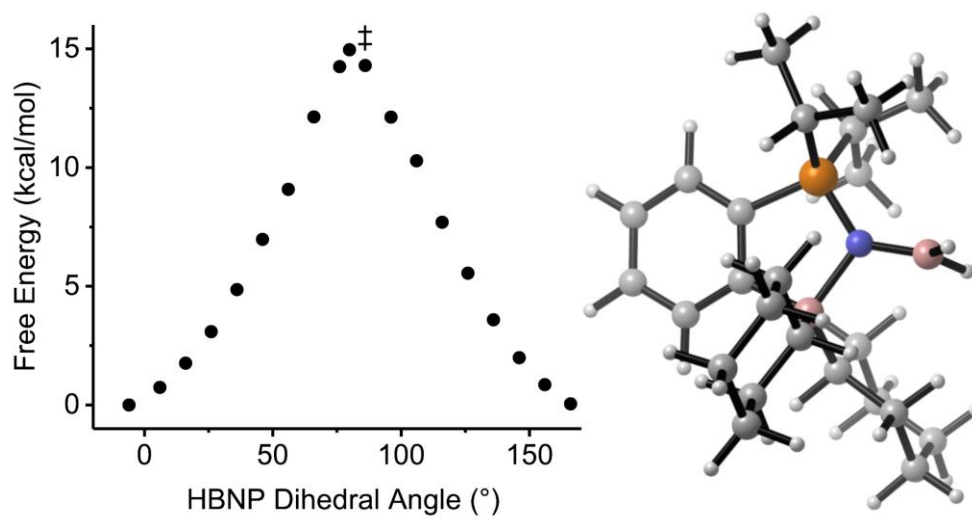


(a)	Bond	Calculated	Experimental
	C1–P1	1.783	1.777(2)
	P1–N1	1.650	1.6538(16)
	N1–B2	1.406	1.396(3)
	B1–N1	1.653	1.659(3)
	C2–B1	1.631	1.630(3)

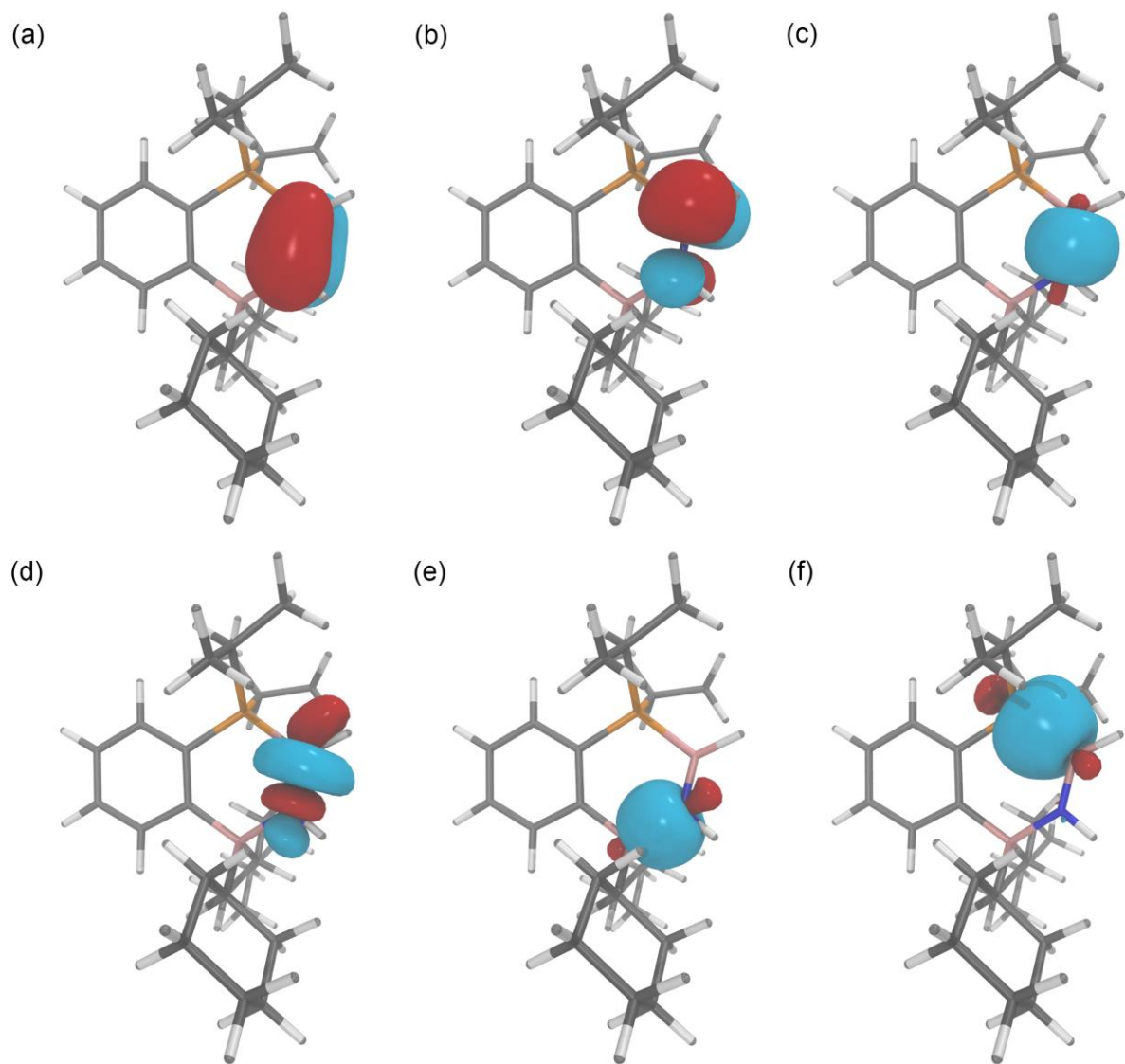
(b)	Bond	WBI	Atom	$Q_{\text{NPA}}$
	C1–P1	0.92	P1	1.90
	P1–N1	0.89	N1	-1.26
	N1–B2	1.07	B2	0.48
	B1–N1	0.93	H1	-0.10
	C2–B1	0.81	H2	-0.07
	-	-	B1	0.74



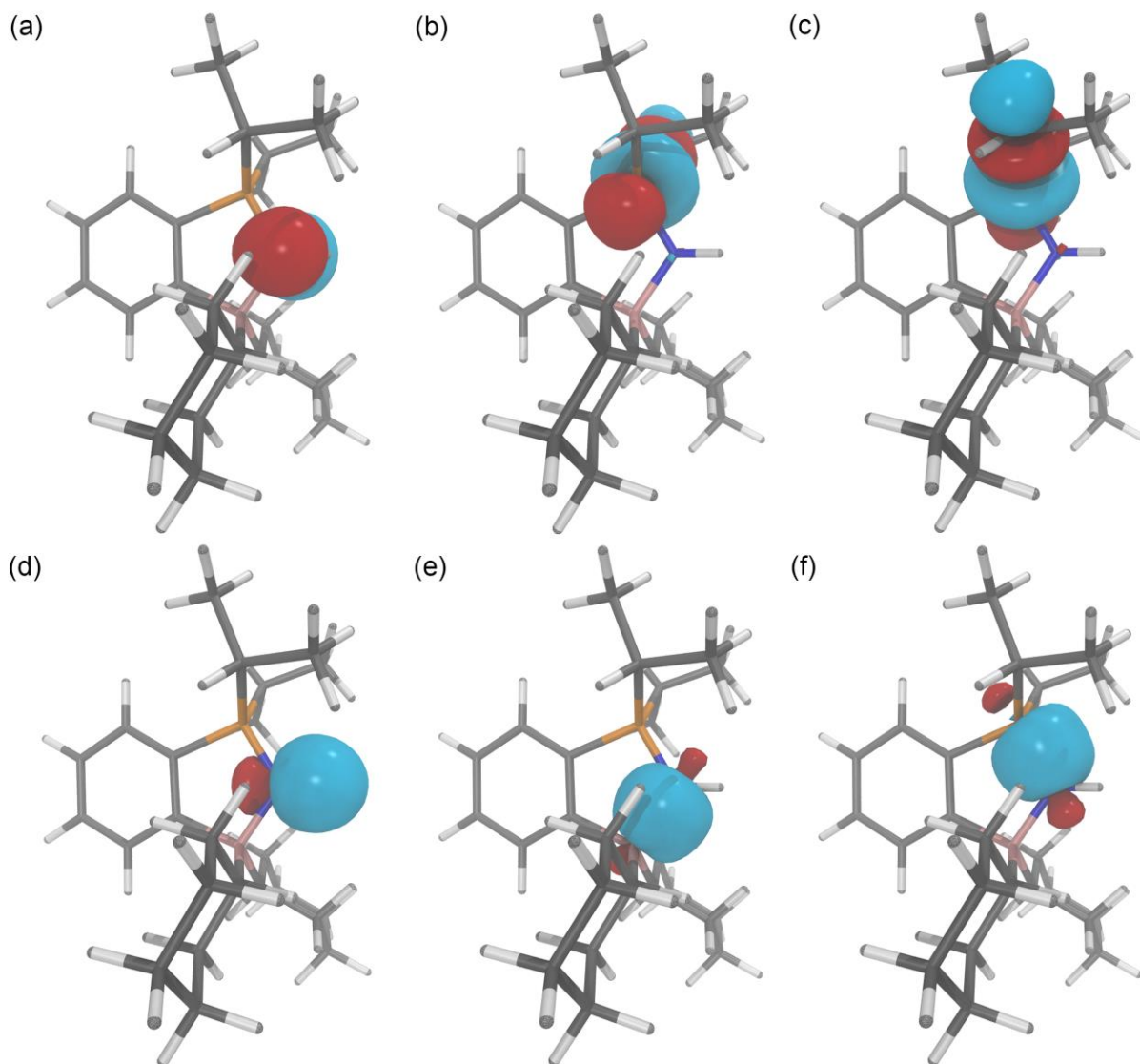
**Fig. S50** HOMO (left) and LUMO (right) of **PB{NH}**.



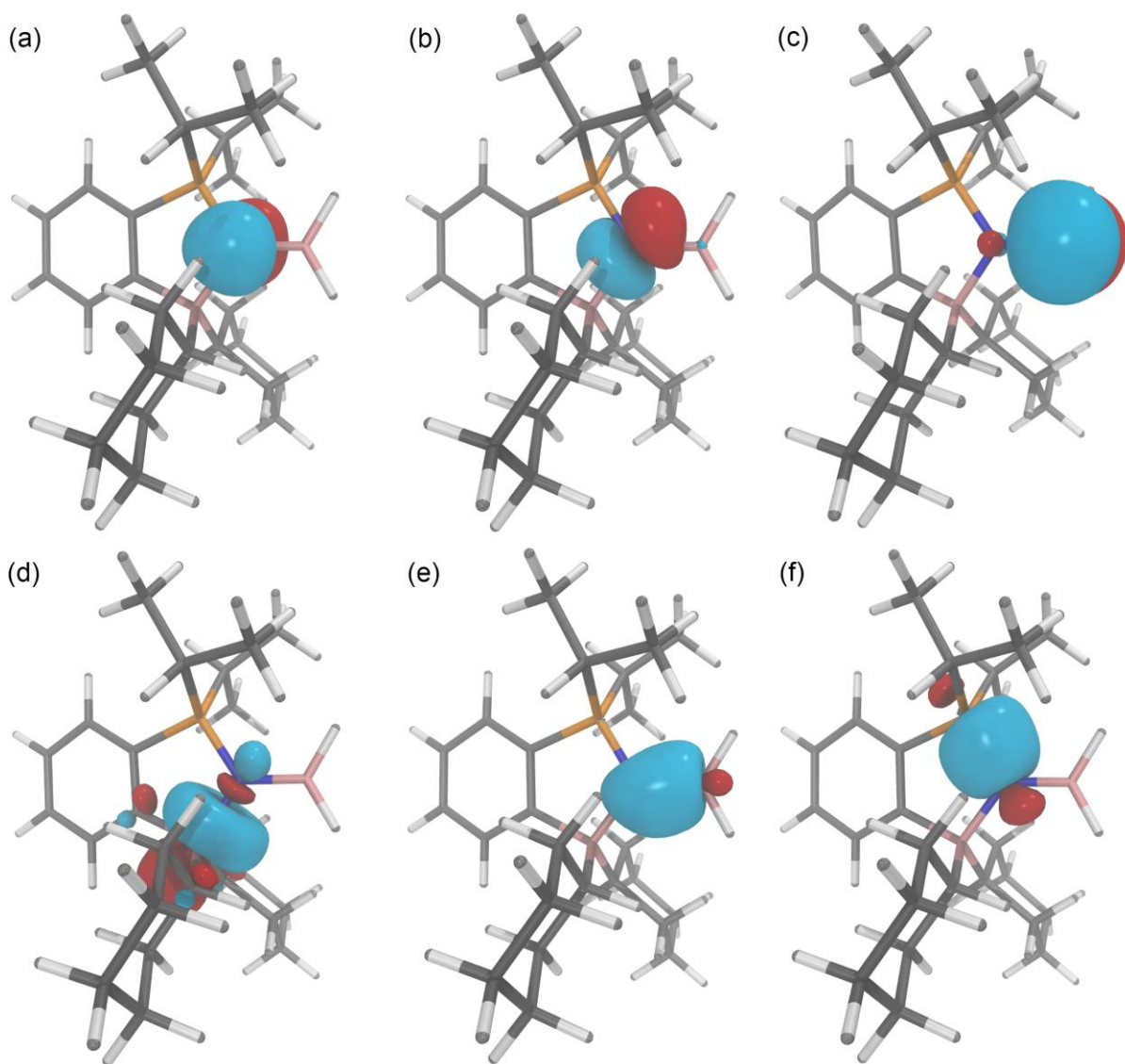
**Fig. S51** Normalized energies of **PB{NBH<sub>2</sub>}** at various fixed dihedral angles and the transition state (‡) for rotation of the exocyclic B–N bond (left) and the transition state (‡) geometry this bond rotation of **PB{NBH<sub>2</sub>}** (right).



**Fig. S52** NBOs of **PB{HBNH}** depicting [with  $e^-$  occupancy]: (a) the B–N  $\pi$  bond [2.0  $e^-$ ]; (b) the B–N  $\pi^*$  orbital [0.0  $e^-$ ]; (c and d) B–N  $\sigma$  and  $\sigma^*$  orbitals [2.0 and 0.0  $e^-$ ]; (e and f) B–N and P–B  $\sigma$  bonds [each 2.0  $e^-$ ].



**Fig. S53** NBOs of PB{NH} depicting [with e<sup>-</sup> occupancy]: (a) a lone pair on N [1.8 e<sup>-</sup>]; (b and c) P-C  $\sigma^*$  orbitals [each 0.1 e<sup>-</sup>]; (d) the N-H  $\sigma$  bond [2.0 e<sup>-</sup>]; (e and f) P-N and B-N  $\sigma$  bonds [each 2.0 e<sup>-</sup>].



**Fig. S54** NBOs of  $\text{PB}\{\text{NBH}_2\}$  depicting [with  $e^-$  occupancy]: (a and b) lone pairs on N [each  $1.7 e^-$ ]; (c and d)  $p$ -orbitals on each B atom [ $0.2$  and  $0.4 e^-$ ]; (e) a B–N  $\sigma$  bond [ $1.9 e^-$ ]; (f) a N–P  $\sigma$  bond [ $2.0 e^-$ ].

**Table S7** Cartesian coordinates for the gas-phase optimized geometry of **PB{NH}**.

P	1.87872	0.17512	-0.36821	C	-3.40731	-3.09441	-0.20154
C	2.83022	-1.26796	-1.01174	H	-4.26534	-3.34691	0.42523
H	2.33232	-2.10468	-0.51677	H	-3.79234	-2.91986	-1.21195
C	4.29573	-1.25319	-0.58137	C	-2.73393	-1.81743	0.30109
H	4.40566	-1.13056	0.49635	H	-2.41677	-1.98190	1.33794
H	4.76389	-2.19916	-0.85460	H	-3.46112	-1.00347	0.32367
H	4.85033	-0.45586	-1.07739	C	-1.91614	1.21606	0.01487
C	2.67618	-1.44935	-2.52158	H	-2.60350	0.98993	0.84461
H	1.62825	-1.48049	-2.81723	C	-2.77490	1.34448	-1.24974
H	3.16878	-0.65446	-3.08057	H	-2.11698	1P.55735	-2.10407
H	3.13286	-2.39362	-2.82003	H	-3.27436	0.40042	-1.47491
C	2.97960	1.64046	-0.45484	C	-3.81958	2.45640	-1.14397
H	3.89296	1.34209	0.06809	H	-4.39119	2.53670	-2.07139
C	2.35194	2.82558	0.27522	H	-4.53206	2.19099	-0.35564
H	2.07725	2.57737	1.29938	C	-3.17984	3.79877	-0.79968
H	3.06236	3.65259	0.29646	H	-3.94505	4.56933	-0.68700
H	1.45388	3.15854	-0.24135	H	-2.53687	4.11031	-1.63017
C	3.31441	2.00367	-1.90174	C	-2.33277	3.69008	0.46584
H	3.91128	1.24130	-2.39895	H	-2.98499	3.46506	1.31601
H	2.40032	2.16032	-2.47826	H	-1.85091	4.64687	0.68085
H	3.87926	2.93594	-1.92381	C	-1.29301	2.57996	0.32413
C	1.36536	-0.10609	1.31786	H	-0.67542	2.52090	1.22536
C	-0.03358	-0.15838	1.37180	H	-0.62134	2.84224	-0.50088
C	-0.58776	-0.31579	2.64669	B	-0.83149	-0.00716	-0.03985
H	-1.66506	-0.33311	2.75906	N	0.41193	0.36320	-1.02137
C	0.21138	-0.43252	3.77353	H	0.29628	0.38799	-2.02266
H	-0.24763	-0.55348	4.74641				
C	1.60095	-0.38384	3.67676				
H	2.21312	-0.46776	4.56398				
C	2.18868	-0.20945	2.43664				
H	3.26701	-0.13920	2.35216				
C	-1.50782	-1.42173	-0.53229				
H	-1.86038	-1.26788	-1.56458				
C	-0.54105	-2.60997	-0.58304				
H	0.30299	-2.37122	-1.23342				
H	-0.12969	-2.78498	0.42003				
C	-1.19849	-3.89792	-1.08068				
H	-1.51501	-3.75542	-2.11949				
H	-0.48090	-4.72194	-1.07843				
C	-2.41924	-4.25654	-0.23873				
H	-2.09455	-4.48034	0.78297				
H	-2.89850	-5.15859	-0.62397				

**Table S8** Cartesian coordinates for the gas phase optimized geometry of **PB{HBNH}**.

P	2.19531	-0.42163	-0.37210	H	4.88837	-1.19602	-1.62140
C	1.25835	-0.31987	1.15800	H	3.58115	-2.08717	-2.40759
C	3.31414	-1.87907	-0.26089	H	4.77274	-2.94178	-1.43057
C	3.19296	1.12395	-0.56472	H	-1.95490	1.67254	-1.45834
B	0.96579	-0.65519	-1.84796	H	0.27543	2.54193	0.40789
C	1.96223	-0.45100	2.36412	H	0.46720	2.15294	-1.30229
C	-0.13180	-0.11568	1.10410	H	0.29212	4.61459	-0.95310
C	-0.75546	-0.02857	2.36366	H	-1.04070	4.00407	-1.92193
B	-1.07848	0.03883	-0.22739	H	-1.13718	4.62409	1.06128
C	-0.07245	-0.13706	3.56009	H	-1.89455	5.57219	-0.20827
C	1.30161	-0.35707	3.57037	H	-3.36578	3.66087	-0.78294
C	4.45713	1.12856	0.29040	H	-3.53873	4.06477	0.91805
C	3.47923	1.43672	-2.03353	H	-3.34710	1.60606	0.60890
C	2.45514	-3.12629	-0.04390	H	-1.98964	2.23370	1.52871
C	4.19027	-2.02289	-1.50529	H	-2.94268	-0.62468	0.84576
C	-1.46407	1.62897	-0.47341	H	-1.52343	-2.73462	-0.81442
C	-0.23941	2.54463	-0.56266	H	-1.36578	-2.53546	0.92005
C	-2.45099	2.22697	0.53443	H	-2.99654	-4.33905	0.35863
C	-0.60176	3.98660	-0.91911	H	-3.77157	-3.02235	1.22504
C	-1.60997	4.55718	0.07564	H	-3.83031	-3.44747	-1.79303
C	-2.84254	3.66215	0.17907	H	-5.17484	-3.71379	-0.69546
C	-2.41207	-0.91650	-0.06971	H	-5.19442	-1.30528	-0.10614
C	-3.43230	-0.75379	-1.20477	H	-5.36506	-1.50466	-1.84285
C	-2.05821	-2.40171	0.08405	H	-3.73452	0.29160	-1.29900
C	-3.28700	-3.28885	0.27982	H	-2.97539	-1.03148	-2.16456
C	-4.28612	-3.10114	-0.85901	N	-0.33386	-0.43036	-1.53317
C	-4.66966	-1.63152	-1.01021	H	1.39569	-0.97910	-2.91170
H	-1.82604	0.11869	2.40016	H	-0.98609	-0.54179	-2.30167
H	-0.61254	-0.06298	4.49523				
H	1.84121	-0.45915	4.50169				
H	3.02876	-0.64132	2.36072				
H	2.50958	1.88452	-0.18099				
H	4.23433	0.97859	1.34579				
H	4.95480	2.09384	0.19170				
H	5.16303	0.36096	-0.02864				
H	2.55847	1.51852	-2.61069				
H	4.10334	0.67537	-2.50074				
H	4.00659	2.38876	-2.10290				
H	3.95148	-1.72304	0.61220				
H	1.83799	-3.04530	0.84965				
H	3.09912	-4.00033	0.05611				
H	1.79378	-3.29133	-0.89699				



**Table S9** Cartesian coordinates for the gas phase optimized geometry of **PB{NBH<sub>2</sub>}**.

P	-1.89191	-0.17182	-0.28547	C	3.35983	3.16940	-0.04555
C	-2.83938	1.35052	-0.69669	H	4.19031	3.42182	0.61721
H	-2.23169	2.12166	-0.21765	H	3.78483	3.00952	-1.04204
C	-4.21502	1.34363	-0.02780	C	2.67676	1.88277	0.41693
H	-4.14668	1.16351	1.04464	H	2.30681	2.04164	1.43678
H	-4.68457	2.31729	-0.16765	H	3.40875	1.07435	0.47285
H	-4.87473	0.59435	-0.46548	C	1.92700	-1.17083	-0.03685
C	-2.92251	1.66918	-2.18757	H	2.52650	-0.98567	0.86851
H	-1.93577	1.75047	-2.63954	C	2.92855	-1.22555	-1.19854
H	-3.48498	0.91933	-2.74137	H	2.39697	-1.45337	-2.12780
H	-3.42701	2.62811	-2.31226	H	3.40420	-0.25425	-1.34685
C	-3.00373	-1.62437	-0.42688	C	4.00015	-2.29480	-0.98088
H	-3.74041	-1.42078	0.35903	H	4.69615	-2.31676	-1.82228
C	-2.24648	-2.90098	-0.06812	H	4.58524	-2.03577	-0.09183
H	-1.73388	-2.81938	0.88886	C	3.37267	-3.67192	-0.78028
H	-2.94995	-3.73219	-0.01608	H	4.14333	-4.42291	-0.59582
H	-1.50357	-3.12985	-0.83113	H	2.85954	-3.96470	-1.70268
C	-3.73731	-1.77848	-1.75842	C	2.36146	-3.64983	0.36316
H	-4.34111	-0.91020	-2.01225	H	2.88796	-3.45045	1.30224
H	-3.03711	-1.96023	-2.57140	H	1.88728	-4.62861	0.46779
H	-4.40374	-2.63926	-1.69250	C	1.31096	-2.56132	0.14579
C	-1.31502	-0.05460	1.39714	H	0.60567	-2.55590	0.98182
C	0.07742	0.08633	1.39434	H	0.73376	-2.81094	-0.75291
C	0.68310	0.16653	2.65459	B	0.83215	0.05163	-0.05057
H	1.76073	0.24882	2.72200	N	-0.43823	-0.25477	-1.06236
C	-0.06255	0.11724	3.82084	B	-0.35018	-0.44768	-2.45199
H	0.43647	0.17924	4.77940	H	0.70455	-0.37659	-2.99266
C	-1.44834	-0.03106	3.78146	H	-1.33319	-0.66553	-3.09788
H	-2.01828	-0.08524	4.69855				
C	-2.08471	-0.12492	2.55808				
H	-3.15778	-0.26961	2.51736				
C	1.49616	1.48488	-0.47976				
H	1.89340	1.35513	-1.49773				
C	0.51530	2.66055	-0.54619				
H	-0.29907	2.42545	-1.23524				
H	0.06535	2.81144	0.44511				
C	1.17600	3.96461	-0.99538				
H	1.52952	3.84214	-2.02441				
H	0.44937	4.78053	-1.00505				
C	2.36252	4.32287	-0.10550				
H	1.99987	4.53143	0.90668				
H	2.84648	5.23386	-0.46258				

**Table S10** Cartesian coordinates for the gas-phase optimized geometry of the **PB{NBH<sub>2</sub>}** exocyclic B–N bond rotation transition state.

P	-1.86510	-0.27448	-0.28329	H	2.41070	5.37278	-0.65102
C	-2.93119	1.12722	-0.82871	C	3.08712	3.38978	-0.09658
H	-2.43310	1.97981	-0.36167	H	3.86815	3.74717	0.57516
C	-4.35223	1.02856	-0.27356	H	3.55987	3.21253	-1.06838
H	-4.36527	0.89968	0.80848	C	2.50283	2.07602	0.42108
H	-4.88955	1.94966	-0.50108	H	2.08230	2.25627	1.41933
H	-4.90075	0.20546	-0.72678	H	3.29913	1.33846	0.54383
C	-2.92273	1.34485	-2.34180	C	2.02372	-1.06414	0.07977
H	-1.91564	1.44640	-2.72609	H	2.62177	-0.81232	0.97500
H	-3.40870	0.53264	-2.87462	C	3.00685	-1.04837	-1.09807
H	-3.46870	2.26438	-2.56760	H	2.47440	-1.25596	-2.03333
C	-2.86813	-1.80808	-0.39545	H	3.44847	-0.05666	-1.21598
H	-3.74234	-1.62165	0.23568	C	4.12367	-2.07617	-0.94121
C	-2.08398	-2.99175	0.16935	H	4.77836	-2.06243	-1.81508
H	-1.71178	-2.79291	1.17354	H	4.73874	-1.80286	-0.08024
H	-2.72429	-3.86864	0.20377	C	3.56690	-3.48044	-0.71788
H	-1.22874	-3.21713	-0.46820	H	4.38188	-4.19840	-0.58004
C	-3.32355	-2.09858	-1.82656	H	3.01555	-3.79165	-1.61007
H	-4.05068	-1.37152	-2.19114	C	2.62279	-3.50243	0.48117
H	-2.47213	-2.10975	-2.51717	H	3.18809	-3.25903	1.38682
H	-3.78467	-3.08339	-1.87007	H	2.21335	-4.50523	0.62280
C	-1.34892	-0.01444	1.40495	C	1.49932	-2.48318	0.30149
C	0.03949	0.14650	1.43971	H	0.82586	-2.50524	1.16294
C	0.60535	0.32924	2.70595	H	0.90480	-2.77706	-0.57003
H	1.67912	0.43670	2.79934	B	0.84744	0.06380	0.03408
C	-0.17808	0.35500	3.84963	N	-0.43016	-0.42460	-1.00032
H	0.28876	0.49309	4.81634	B	-0.08219	-0.71348	-2.35931
C	-1.55903	0.18979	3.77525	H	0.58854	-1.72654	-2.58967
H	-2.15929	0.19875	4.67443	H	-0.44962	0.02228	-3.29812
C	-2.15452	-0.00283	2.54102				
H	-3.22420	-0.16154	2.47602				
C	1.38538	1.52185	-0.48375				
H	1.82848	1.37417	-1.48054				
C	0.31458	2.60295	-0.65412				
H	-0.44983	2.25130	-1.35468				
H	-0.18586	2.76958	0.30977				
C	0.87801	3.93139	-1.15982				
H	1.27835	3.78139	-2.16796				
H	0.08469	4.67795	-1.24281				
C	1.99523	4.44393	-0.25590				
H	1.57925	4.67584	0.73029				

## 6. Infrared spectra

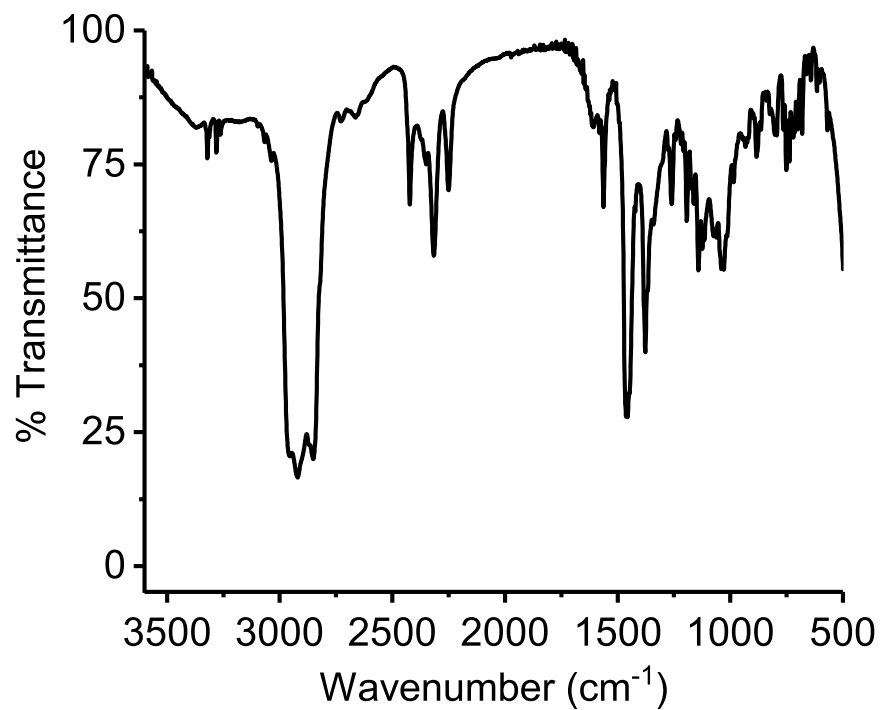


Fig. S55 IR spectrum (Nujol mull) of PB{H<sub>2</sub>BNH<sub>2</sub>}.

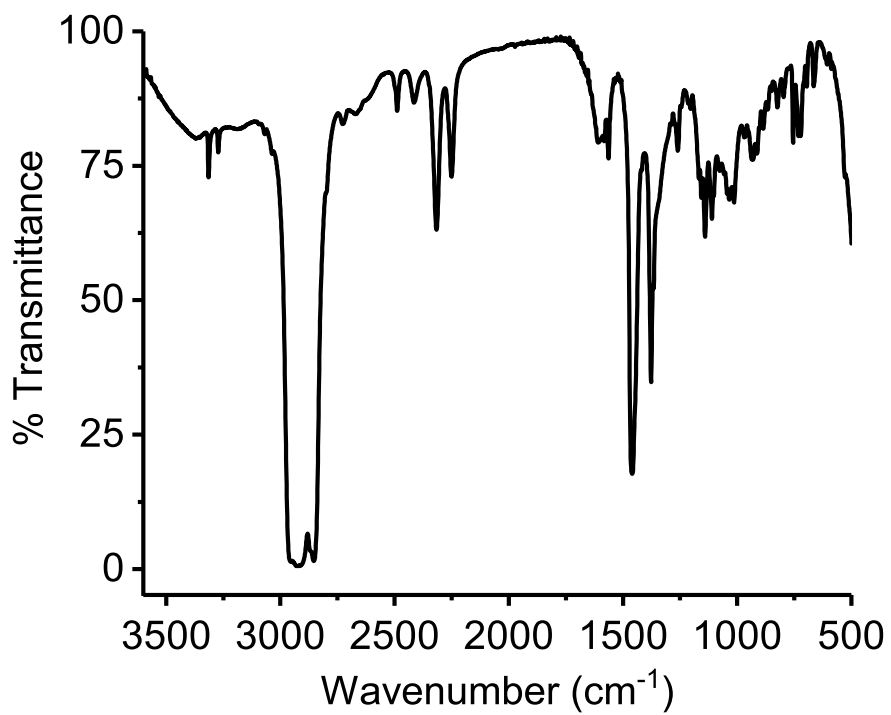
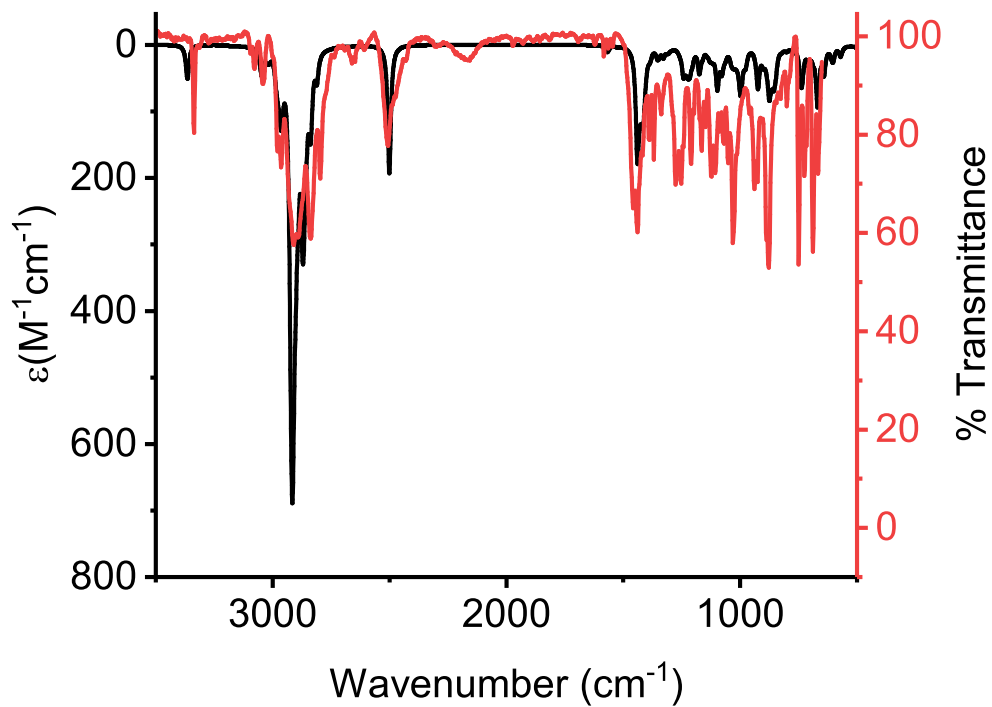
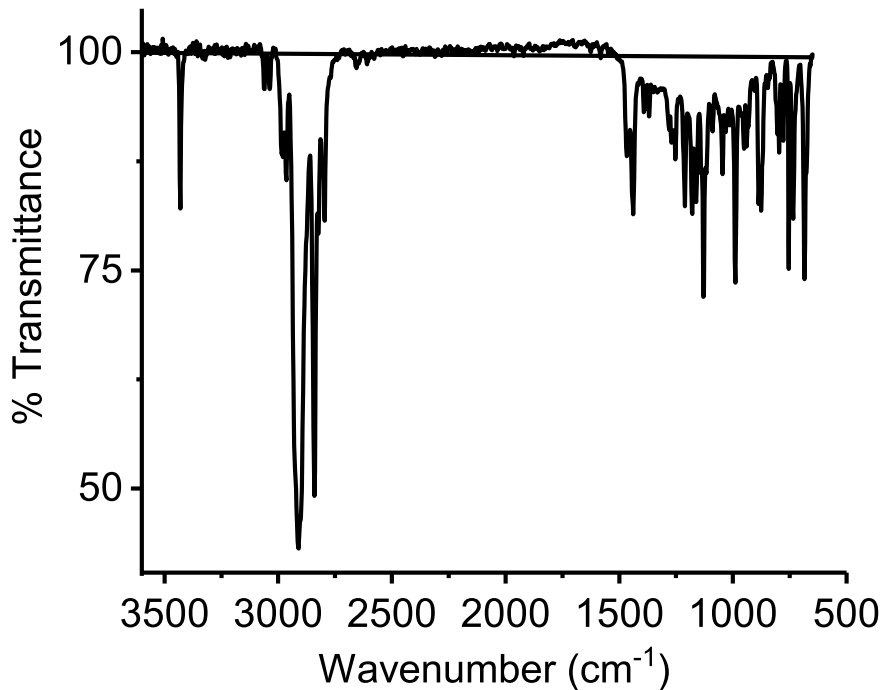


Fig. S56 IR spectrum (Nujol mull) of PB{H(I)BNH<sub>2</sub>}.



**Fig. S57** Computed (black trace) and measured (red trace) IR spectra (powder, KBr plate) of **PB{HBNH}**.



**Fig. S58** IR Spectrum ( $\text{CH}_2\text{Cl}_2$  dropcast, KBr plate) of **PB{NH}**.

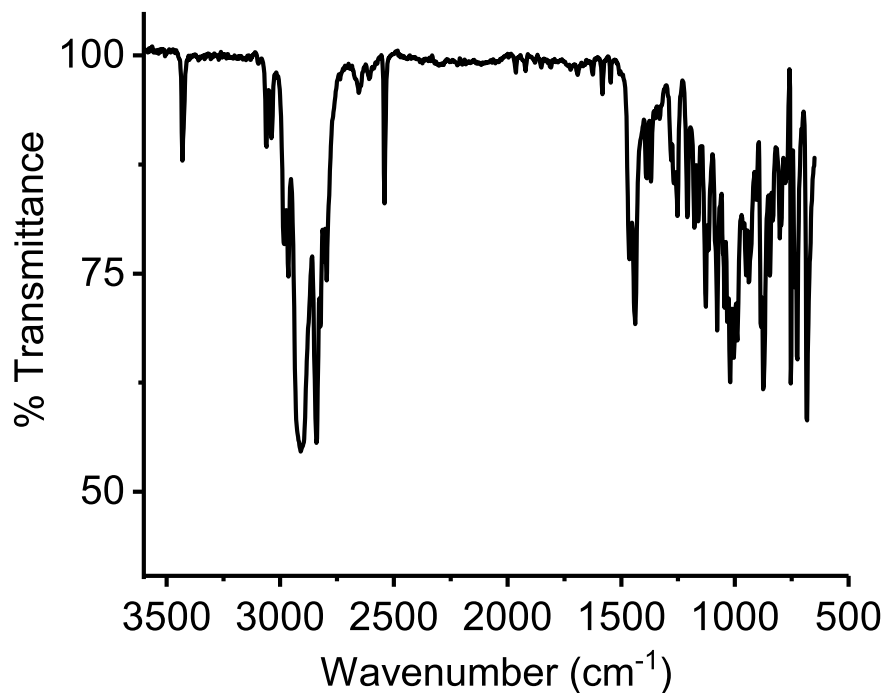


Fig. S59 IR spectrum (powder, KBr plate) of PB{ND}.

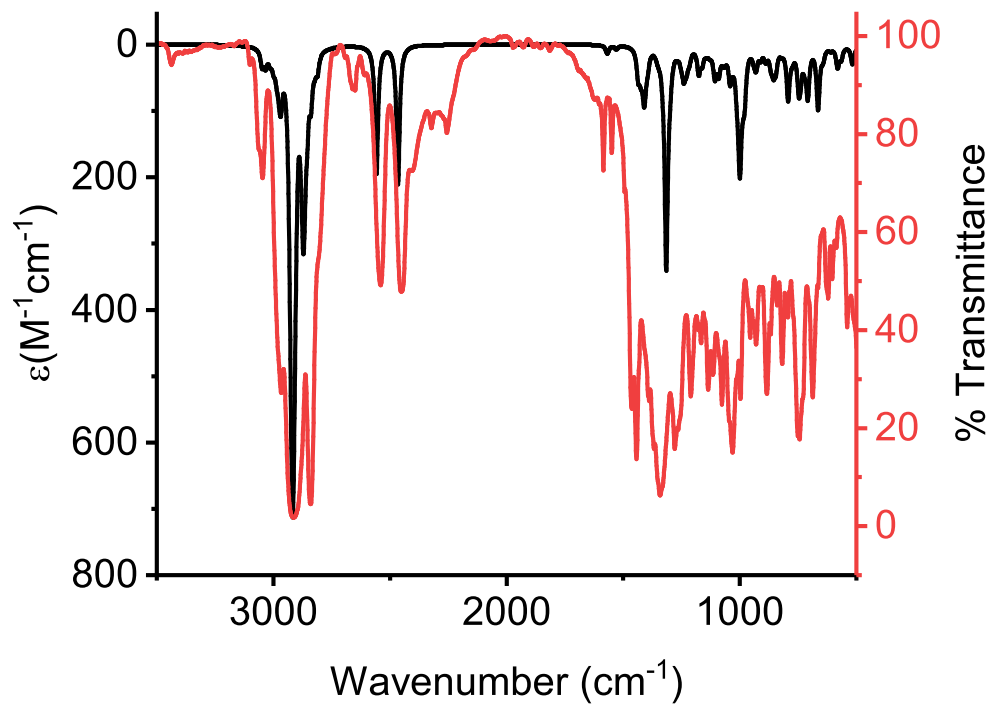


Fig. S56 Computed (black trace) and measured (red trace) IR spectra (CH<sub>2</sub>Cl<sub>2</sub> dropcast, KBr plate) of PB{NBH<sub>2</sub>}.

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