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## **Supplementary Information for**

### Solid State frustrated Lewis pair chemistry

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# Supplementary Information (Part 1. Experimental and Analytical Details)

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#### **Materials and Methods**

All experiments were carried out in a dry argon atmosphere using an MBraun glove box and/or standard Schlenk techniques. All solvents were dried and stored under an argon atmosphere before use. NMR spectra were measured on a Varian INOVA 500 MHz spectrometer (<sup>1</sup>H 500 MHz; <sup>13</sup>C, 126 Hz; <sup>11</sup>B, 160 MHz; <sup>19</sup>F, 470 Hz) or a Varian UNITY plus 600 MHz spectrometer (<sup>1</sup>H 600 MHz; <sup>13</sup>C, 151 Hz; <sup>11</sup>B, 192 MHz; <sup>19</sup>F, 564 Hz). Chemical shifts are given relative to SiMe<sub>4</sub> and referenced to the respective residual solvent signal (<sup>1</sup>H NMR and <sup>13</sup>C NMR) or an external standard [ $\delta$  (BF<sub>3</sub>·OEt<sub>2</sub>) = 0 for <sup>11</sup>B NMR,  $\delta$  (CFCl<sub>3</sub>) = 0 for <sup>19</sup>F NMR]. NMR assignments were supported by additional 1D and 2D NMR experiments.

Compounds 1a, 1b, 1c were bought from Sigma-Aldrich and used without further purification (stored in glove box to avoid moisture and air). Compound 2 was purchased from Boulder Scientific, purified by recrystallization in pentane and then sublimation before use. SO<sub>2</sub> gas was commercially available and further dried by passing through a column of  $P_4O_{10}$ . Fluorous solvent perfluoro(methylcyclohexane) was bought from Sigma-Aldrich (technical grade, 90%) and used without further purification (stored in glove box to avoid moisture and air). Unless otherwise noted, all chemicals were purchased from commercially available sources.

**X-Ray diffraction:** For compound **5a** data sets were collected with a Kappa CCD APEXII Bruker diffractometer. For compounds 4a and 3b data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., 2014); cell refinement: SAINT V8.34A (Bruker AXS Inc., 2013); data reduction: SAINT V8.34A (Bruker AXS Inc., 2013); absorption correction, SADABS V2014/2 (Bruker AXS Inc., 2014); structure solution SHELXT-2014 (Sheldrick, 2014); structure refinement SHELXL-2014 (Sheldrick, 2014) and graphics, XP (Bruker AXS Inc., 2014). R-values are given for observed reflections, and  $wR^2$  values are given for all reflections. *Exceptions and special features*: For compound 4a one additional dichloromethane molecule disordered over two positions was found in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability of the compound. For compound **5a** one half badly disordered hexane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters do not include the squeezed solvent molecule.

1) Reactions of  $PCy_3$  (1a) with  $B(C_6F_5)_3$ 

<u>1.1) Reaction of PCy<sub>3</sub> (1a) with  $B(C_6F_5)_3$  in a H<sub>2</sub> atmosphere in the solid state: preparation of compound 4a and control mixture sample</u>

$$B(C_6F_5)_3 + PCy_3 \xrightarrow{H_2 (50 \text{ bar})} HPCy_3 / HB(C_6F_5)_3$$
  
solid state  
**1a 4a**

Scheme S1. Reaction of  $PCy_3$  (1a) with  $B(C_6F_5)_3$  in the solid state: preparation of compound 4a

A mixture of  $B(C_6F_5)_3$  (102.4 mg, 0.2 mmol) and  $PCy_3$  (56.1 mg, 0.2 mmol) was put in a vial with a double valve adaptor<sup>a</sup> and stirred for 15 min. Then the reaction mixture was stirred in a dihydrogen atmosphere (50 bar) for 10 days. After the reaction time the obtained powder was characterized by NMR experiments in solution (>90% conversion) and in the solid state.<sup>1</sup>

The obtained NMR data of the obtained powder in solution (dichloromethane- $d_2$ ) were consistent to those given for the isolated compound **4a** (see below).

\*Control mixture sample: A mixture of  $B(C_6F_5)_3$  (102.4 mg, 0.2 mmol) and  $PCy_3$  (56.1 mg, 0.2 mmol) was put in a vial with a double valve adaptor and stirred for 10 days in a argon atmosphere. The obtained control mixture sample was characterized by NMR experiments in the solid state.

# <u>1.2) Reaction of PCy<sub>3</sub> (1a) with $B(C_6F_5)_3$ in a H<sub>2</sub> atmosphere in the solid state: isolation of compound 4a</u>

A mixture of  $B(C_6F_5)_3$  (102.4 mg, 0.2 mmol) and  $PCy_3$  (56.1 mg, 0.2 mmol) were put in a vial with a double valve adaptor<sup>a</sup> and stirred for 15 min. Then the reaction mixture was stirred in a dihydrogen atmosphere (50 bar) for 10 days. After the reaction time the obtained powder was crystallized from dichloromethane/pentane and dried in vacuo to give a white solid (128.3 mg, 0.162 mmol, 81 %).<sup>1</sup> [Cy: cyclohexyl]

<sup>1</sup>**H** NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta = 5.15$  (dq, <sup>1</sup>*J*<sub>PH</sub> = 444.0 Hz, <sup>3</sup>*J*<sub>HH</sub> = 4.1 Hz, 1H, PH), 3.59 (br 1:1:1:1 q, <sup>1</sup>*J*<sub>BH</sub> ~ 92 Hz, 1H, BH), 2.43 (m, 3H, CH<sup>Cy</sup>), 1.96/1.55, 1.93/1.40 (each m, each 6H, CH<sub>2</sub><sup>Cy</sup>), 1.82/1.31 (each m, each 3H, CH<sub>2</sub><sup>Cy</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 148.6 (dm, <sup>1</sup>J<sub>FC</sub> ~ 235 Hz, C<sub>6</sub>F<sub>5</sub>), 138.1 (dm, <sup>1</sup>J<sub>FC</sub> ~ 240 Hz, C<sub>6</sub>F<sub>5</sub>), 136.8 (dm, <sup>1</sup>J<sub>FC</sub> ~ 245 Hz, C<sub>6</sub>F<sub>5</sub>), 125.5 (br, i-C<sub>6</sub>F<sub>5</sub>), 28.5 (d, <sup>1</sup>J<sub>PC</sub> = 38.3 Hz, CH<sup>Cy</sup>), 28.4 (d, J<sub>PC</sub> = 3.9 Hz), 26.4 (d, J<sub>PC</sub> = 12.7 Hz), 25.2 (d, J<sub>PC</sub> = 1.6 Hz)(CH<sub>2</sub><sup>Cy</sup>).

<sup>11</sup>**B** NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -25.3 (d, <sup>1</sup>*J*<sub>BH</sub> ~ 92 Hz). <sup>11</sup>**B**{<sup>1</sup>**H**} NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -25.3 (v<sub>1/2</sub> ~ 40 Hz).

<sup>19</sup>**F** NMR (470 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -133.9 (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>), -164.6 (t, <sup>3</sup>J<sub>FF</sub> = 20.2 Hz, 1F, *p*-C<sub>6</sub>F<sub>5</sub>), -167.5 (m, 2F, *m*-C<sub>6</sub>F<sub>5</sub>), [Δδ<sup>19</sup>Fm,p = 2.9].

<sup>31</sup>**P** NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 33.2 (br d, <sup>1</sup>*J*<sub>PH</sub> ~ 443 Hz).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 33.2 (v<sub>1/2</sub> ~ 3 Hz).



6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 0.0 Figure S1. <sup>1</sup>**H NMR** (500 MHz, 299K, dichloromethane- $d_2^*$ ) spectra of (1) the obtained powder (see experiment 1.1) and (2) the isolated compound **4a** (see experiment 1.2).



150 140 130 120 110 100 90 80 70 60 50 40 30 20 Figure S2.  ${}^{13}C{}^{1}H$  (126 MHz, 299K, dichloromethane-d<sub>2</sub>) spectrum of the isolated compound **4a** (see experiment 1.2).



-130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 Figure S4. <sup>19</sup>**F** NMR (470 MHz, 299K, dichloromethane- $d_2$ ) spectra of (1) the obtained powder (see experiment 1.1) and (2) the isolated compound **4a** (see experiment 1.2).



Figure S5. (1,3)  ${}^{31}P{}^{1}H$  and (2,4)  ${}^{31}P$  NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained powder (see experiment 1.1) and (3,4) the isolated compound **4a** (see experiment 1.2).

Single crystals of compound **4a** suitable for the X-ray crystal structure analysis were obtained of diffusion of pentane to a solution of compound **3a** in dichloromethane at -36 <sup>o</sup>C. [X-ray crystal structure analysis see: Jiang, Y., Schirmer, B., Blacque, O., Fox, T., Grimme, S., and Berke, H. (2013). The "Catalytic Nitrosyl Effect": NO Bending Boosting the Efficiency of Rhenium Based Alkene Hydrogenations. J. Am. Chem. Soc. *135*, 4088-4102.].<sup>2</sup>

**X-ray crystal structure analysis of compound 4a:** A colorless needle-like specimen of  $C_{36}H_{35}BF_{15}P$ , approximate dimensions 0.010 mm x 0.030 mm x 0.260 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2003 frames were collected. The total exposure time was 49.19 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 39592 reflections to a maximum  $\theta$  angle of 65.07° (0.85 Å resolution), of which 5803 were independent (average redundancy 6.823, completeness = 99.7%,  $R_{int} = 15.69\%$ ,  $R_{sig} = 10.91\%$ ) and 3530 (60.83%) were greater than  $2\sigma(F^2)$ . The final cell constants of <u>a</u> = 28.898(3) Å, <u>b</u> = 11.2532(9) Å, c = 21.7565(19) Å,  $\beta = 105.318(5)^{\circ}$ , volume = 6823.8(10) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 4821 reflections above 20  $\sigma(I)$  with 8.427°  $< 2\theta < 131.8^{\circ}$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.764. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6640 and 0.9830. The final anisotropic full-matrix least-squares refinement on  $F^2$  with 486 variables converged at R1 = 11.55%, for the observed data and wR2 = 33.37% for all

data. The goodness-of-fit was 1.019. The largest peak in the final difference electron density synthesis was 1.163  $e^{-1}/A^3$  and the largest hole was -0.506  $e^{-1}/A^3$  with an RMS deviation of 0.109  $e^{-1}/A^3$ . On the basis of the final model, the calculated density was 1.547 g/cm<sup>3</sup> and F(000), 3248  $e^{-1}$ .



Figure S6. X-ray crystal structure analysis of compound 4a.

1.3) Reaction of PCy<sub>3</sub> (1a) with  $B(C_6F_{5)3}$  in solution: preparation of compound 3a



Scheme S2. Reaction of  $PCy_3$  (1a) with  $B(C_6F_5)_3$  in solution: preparation of compound 3a.

A solution of PCy<sub>3</sub> (84.1 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added to a solution of  $B(C_6F_5)_3$  (153.6 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The mixture was stirred at room temperature for 12 hours. Then all volatiles were removed in vacuo to give a white solid, which was washed with pentane (1mL × 3) and dried in vacuo to finally give compound **3a** as a white solid (204.1 mg, 0.258 mmol, 86 %).<sup>3</sup> The white solid was also measured by solid state NMR.

<sup>1</sup>**H** NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta = 2.92$  (m, 1H, CH<sup>Cy</sup>), 1.99/1.57, 1.96/1.41 (each br m, each 2H, CH<sub>2</sub><sup>Cy</sup>), 1.84/1.34 (each br m, each 1H, CH<sub>2</sub><sup>Cy</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta = 33.1$  (dt, <sup>1</sup>*J*<sub>PC</sub> = 38.6 Hz, *J* = 4.2 Hz, CH<sup>Cy</sup>), 27.9 (d, *J*<sub>PC</sub> = 3.8 Hz), 27.3 (d, *J*<sub>PC</sub> = 12.9 Hz), 25.7 (d, *J*<sub>PC</sub> = 1.8 Hz)(CH<sub>2</sub><sup>Cy</sup>), [C<sub>6</sub>F<sub>5</sub> and C<sub>6</sub>F<sub>4</sub> not listed].

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -0.6 (d, <sup>1</sup>*J*<sub>FB</sub> ~ 67 Hz).

<sup>19</sup>**F** NMR (470 MHz, 299K, dichloromethane-d<sub>2</sub>) δ = -128.3, -131.7 (each m, each 2F, C<sub>6</sub>F<sub>4</sub>), - 135.5 (m, 4F, *o*), -161.6 (t,  ${}^{3}J_{FF}$  = 20.0 Hz, 2F, *p*), -166.5 (m, 4F, *m*)(C<sub>6</sub>F<sub>5</sub>) [Δδ<sup>19</sup>F<sub>m,p</sub> = 4.9], 193.0 (br m, BF).

<sup>31</sup>**P**{<sup>1</sup>**H**} **NMR** (202 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 41.0 (m).



5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 Figure S7. <sup>1</sup>**H NMR** (500 MHz, 299K, dichloromethane-d<sub>2</sub>) spectrum of compound **3a**.



240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 Figure S8.  ${}^{13}C{}^{1}H$  NMR (126 MHz, 299K, dichloromethane-d<sub>2</sub>) spectrum of compound **3a** 









Single crystals suitable for the X-ray crystal structure analysis were obtained by pentane diffusion to a solution of compound 3a in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 3a: A colorless prism-like specimen of C<sub>36</sub>H<sub>33</sub>BF<sub>15</sub>P · 2 x CH<sub>2</sub>Cl<sub>2</sub> approximate dimensions 0.098 mm x 0.196 mm x 0.219 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 984 frames were collected. The total exposure time was 16.40 hours. The frames were integrated with the Bruker SAINT software package using a narrowframe algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 194744 reflections to a maximum  $\theta$  angle of 26.37° (0.80 Å resolution), of which 8145 were independent (average redundancy 23.910, completeness = 99.9%, R<sub>int</sub> = 5.16%,  $R_{sig} = 1.41\%$ ) and 6970 (85.57%) were greater than  $2\sigma(F^2)$ . The final cell constants of <u>a</u> = 20.8497(8) Å, <u>b</u> = 16.0333(6) Å, <u>c</u> = 23.8954(9) Å, volume = 7988.0(5) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9344 reflections above 20  $\sigma(I)$ with  $4.962^{\circ} < 2\theta < 55.01^{\circ}$ . Data were corrected for absorption effects using the multiscan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.948. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9100 and 0.9580. The final anisotropic full-matrix least-squares refinement on  $F^2$  with 560 variables converged at R1 = 4.05%, for the observed data and wR2 = 10.73% for all data. The goodness-of-fit was 1.047. The largest peak in the final difference electron density synthesis was 0.653 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -0.742 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.066  $e^{-}/Å^{3}$ . On the basis of the final model, the calculated density was  $1.600 \text{ g/cm}^3$  and F(000), 3904 e<sup>-</sup>.



Figure S12. X-ray crystal structure analysis of compound **3a**.

<u>1.4) Reaction of PCy<sub>3</sub> (1a) with  $B(C_6F_5)_3$  in solution in a H<sub>2</sub> atmosphere: generation of compound 3a</u>



Scheme S3. Reaction of  $PCy_3$  (1a) with  $B(C_6F_5)_3$  in solution in a  $H_2$  atmosphere: generation of compound 3a

A solution of PCy<sub>3</sub> (14.0 mg, 0.05 mmol) and  $B(C_6F_5)_3$  (25.6 mg, 0.05 mmol) in  $CD_2Cl_2$  (1 mL) was put in a vial with a double valve adaptor<sup>a</sup> and stirred for 12 hours in an H<sub>2</sub> atmosphere (50 bar). Then the reaction solution was characterized by NMR experiments.<sup>1</sup>

[Comment: the obtained NMR data were consistent to those given for compound **3a** (see experiment 1.3)]



00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 Figure S14.  ${}^{11}B{}^{1}H{}$  NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the reaction mixture and (2) the isolated compound **3a** (see experiment 1.3).



(2) the isolated compound **3a** (see experiment 1.3).

2) Reactions of PhPCy<sub>2</sub> (**1b**) with  $B(C_6F_5)_3$ 2.1) Reaction of PhPCy<sub>2</sub> (**1b**) with  $B(C_6F_5)_3$  in a H<sub>2</sub> atmosphere in the solid state: preparation of compound **4b** 

$$B(C_6F_5)_3 + PPhCy_2 \xrightarrow{H_2 (50 \text{ bar})} HPPhCy_2 / HB(C_6F_5)_3$$
  
solid state  
**1b 4b**

Scheme S4. Reaction of PhPCy<sub>2</sub> (**1b**) with  $B(C_6F_5)_3$  in the solid state: preparation of compound **4b**.

A mixture of  $B(C_6F_5)_3$  (102.4 mg, 0.2 mmol) and PhPCy<sub>2</sub> (54.8 mg, 0.2 mmol) was put in a vial with a double valve adaptor<sup>a</sup> and stirred for 15 min. Then the reaction mixture was stirred in a dihydrogen atmosphere (50 bar) for 3 days. After the reaction time a part of the obtained powder (30 mg) was characterized by NMR experiments in solution (ca. 95% conversion).<sup>1</sup>

The remaining solid was crystallized from dichloromethane/pentane and dried in vacuo to give compound **4b** as a white solid (111.6 mg, 0.142 mmol, yield 71 %).

<sup>1</sup>**H** NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>) δ = 7.88 (m, 1H, *p*-Ph), 7.72 (m, 2H, *m*-Ph), 7.62 (m, 2H, *o*-Ph), 6.13 (dt, <sup>1</sup>*J*<sub>PH</sub> = 459.3 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.2 Hz, PH), 3.64 (br 1:1:1:1 q, <sup>1</sup>*J*<sub>BH</sub> ~ 95 Hz, BH), 2.63 (m, 2H, CH<sup>Cy</sup>), 2.03/1.36, 1.90/1.42, 1.86/1.37, 1.84/1.32, 1.77/1.21 (each m, each 2H, CH<sub>2</sub><sup>Cy</sup>)<sup>a</sup>. [<sup>a</sup> from the <sup>1</sup>H, <sup>13</sup>C ghsqc experiment]. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299K, dichloromethane-d<sub>2</sub>) δ = 136.4 (d, <sup>4</sup>*J*<sub>PC</sub> = 2.9 Hz, *p*-Ph), 133.8 (d, <sup>2</sup>*J*<sub>PC</sub> = 12.4 Hz, *o*-Ph), 131.3 (d, <sup>3</sup>*J*<sub>PC</sub> = 8.8 Hz, *m*-Ph), 111.3 (d, <sup>1</sup>*J*<sub>PC</sub> = 76.8 Hz, *i*-Ph), 29.2 (d, <sup>1</sup>*J*<sub>PC</sub> = 41.1 Hz, CH<sup>Cy</sup>), 27.7 (d, *J*<sub>PC</sub> = 3.2 Hz), 26.7 (d, *J*<sub>PC</sub> = 3.6 Hz), 26.0 (d, *J*<sub>PC</sub> = 8.1 Hz), 25.9 (d, *J*<sub>PC</sub> = 7.8 Hz), 25.1 (d, *J*<sub>PC</sub> = 1.6 Hz)(CH<sub>2</sub><sup>Cy</sup>), [C<sub>6</sub>F<sub>5</sub> not listed]. <sup>11</sup>B NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) δ = -25.3 (d, <sup>1</sup>*J*<sub>BH</sub> ~ 94 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) δ = -25.3 (w<sub>1/2</sub> ~ 40 Hz). <sup>13</sup>FF = 20.2 Hz, 1F, *p*-C<sub>6</sub>F<sub>5</sub>), -167.5 (m, 2F, *m*-C<sub>6</sub>F<sub>5</sub>), [Δδ<sup>19</sup>F<sub>m,p</sub> = 3.0]. <sup>31</sup>P NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) δ = 30.6 (br d, <sup>1</sup>*J*<sub>PH</sub> ~ 461 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) δ = 30.6 (v<sub>1/2</sub> ~ 5 Hz).



8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 Figure S18. <sup>1</sup>H NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the obtained powder and (2) the isolated compound **4b**.





<sup>100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40</sup> Figure S20. (1,3) <sup>11</sup>**B**{<sup>1</sup>**H**} and (2,4) <sup>11</sup>**B** NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained powder and (3,4) the isolated compound 4b.







30 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20Figure S22. (1,3)  ${}^{31}P{}^{1}H{}$  and (2,4)  ${}^{31}P$  NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained powder and (3,4) the isolated compound 4b. 2.2) Reaction of PhPCy<sub>2</sub> (1b) with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in solution: generation of compound 3b



Scheme S5. Reaction of PhPCy<sub>2</sub> (**1b**) with  $B(C_6F_5)_3$  in solution: generation of compound **3b**.

A solution of PhPCy<sub>2</sub> (82.3 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added to a solution of  $B(C_6F_5)_3$  (153.6 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). After the mixture was stirred at room temperature for 12 hours, all volatiles were removed in vacuo to give a white solid which was washed with pentane (1mL × 3) and dried in vacuo to finally give compound **3b** as a white solid (193.2 mg, 0.246 mmol, 82 %).

<sup>1</sup>**H** NMR (600 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 7.86 (m, 1H, *p*-Ph), 7.73 (m, 2H, *m*-Ph), 7.58 (m, 2H, *o*-Ph), 3.06 (m, 2H, CH<sup>Cy</sup>), 2.01/1.24, 1.97/1.05, 1.94, 1.89, 1.49, 1.45, 1.76/1.12 (each m, each 2H, CH<sub>2</sub><sup>Cy</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 135.6 (d, <sup>4</sup>*J*<sub>PC</sub> = 3.1 Hz, *p*-Ph), 132.8 (d, <sup>2</sup>*J*<sub>PC</sub> = 8.4 Hz, *o*-Ph), 130.5 (d, <sup>3</sup>*J*<sub>PC</sub> = 12.2 Hz, *m*-Ph), 113.1 (d, <sup>1</sup>*J*<sub>PC</sub> = 80.3 Hz, *i*-Ph), 31.2 (d, <sup>1</sup>*J*<sub>PC</sub> = 43.9 Hz, CH<sup>Cy</sup>), 26.23 (d, *J*<sub>PC</sub> = 13.6 Hz), 26.17 (d, *J*<sub>PC</sub> = 14.2 Hz), 25.8 (d, *J*<sub>PC</sub> = 3.9 Hz), 25.7 (d, *J*<sub>PC</sub> = 3.2 Hz), 25.3 (d, *J*<sub>PC</sub> = 1.6 Hz)(CH<sub>2</sub><sup>Cy</sup>), [C<sub>6</sub>F<sub>5</sub> and C<sub>6</sub>F<sub>4</sub> not listed].

<sup>11</sup>B{<sup>1</sup>H} NMR (192 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -0.6 (br d, <sup>1</sup>*J*<sub>FB</sub> ~ 70 Hz). <sup>19</sup>F NMR (564 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -127.5 (br), -128.4 (br m)(each 2F, C<sub>6</sub>F<sub>4</sub>), -135.5 (m, 4F, *o*), -161.6 (m, <sup>3</sup>*J*<sub>FF</sub> = 20.1 Hz, 2F, *p*), -166.5 (m, 4F, *m*)(C<sub>6</sub>F<sub>5</sub>) [ $\Delta \delta^{19}F_{m,p} = 4.9$ ], -192.9 (br m, 1F, BF).

<sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 33.6 (m).





90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 Figure S25. (1)  ${}^{11}B{}^{1}H{}$  and (2)  ${}^{11}B NMR$  (192 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of compound **3b**.



34.6 34.2 33.8 33.4 33.0 32.6 32.2 31.8 31.4 31.0 30.6 30.2 29.8 29.4 29.0 28.6 Figure S27. (1)  ${}^{31}P{}^{1}H{}$  and (2)  ${}^{31}P$  NMR (243 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of compound **3b**.

# 2.3) Reaction of PhPCy<sub>2</sub> (**1b**) with $B(C_6F_5)_3$ in solution in a $H_2$ atmosphere: generation of a mixture of compounds **3b** and **4b**

A solution of PhPCy<sub>2</sub> (13.7 mg, 0.05 mmol) and  $B(C_6F_5)_3$  (25.6 mg, 0.05 mmol) in  $CD_2Cl_2$  (1 mL) was put in a vial with a double valve adaptor<sup>a</sup> and stirred for 12 hours in an H<sub>2</sub> atmosphere (50 bar). Then the reaction solution was characterized by NMR experiments.<sup>1</sup>

[Comment: the obtained NMR data showed a mixture of compounds **3b** and **4b** (ratio ca. 6:1 (<sup>1</sup>H)]



8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 Figure S28. (1,3) <sup>1</sup>**H** NMR (500 MHz) and (2) <sup>1</sup>**H** NMR (600 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the obtained reaction mixture, (2) the isolated compound **3b** and (3) the isolated compound **4b**.



<sup>95</sup> <sup>85</sup> <sup>75</sup> <sup>65</sup> <sup>55</sup> <sup>45</sup> <sup>35</sup> <sup>25</sup> <sup>15</sup> <sup>5</sup> <sup>-5</sup> <sup>-5</sup> <sup>-15</sup> <sup>-25</sup> <sup>-35</sup> Figure S29. (1,5) <sup>11</sup>B{<sup>1</sup>H}/(2,6) <sup>11</sup>B NMR (160 MHz) and (3) <sup>11</sup>B{<sup>1</sup>H}/(4) <sup>11</sup>B NMR (192 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained reaction mixture, (3,4) the isolated compound **3b** and (5,6) the isolated compound **4b**.



36 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 Figure S31. (1,5) <sup>31</sup>P{<sup>1</sup>H}/ (2,6) <sup>31</sup>P NMR (202 MHz) and (3) <sup>31</sup>P{<sup>1</sup>H}/ (4) <sup>31</sup>P NMR (243 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained reaction mixture, (3,4) the isolated compound **3b** and (5,6) the isolated compound **4b**.

3) Reactions of  $Ph_2P^tBu$  (1c) with  $B(C_6F_5)_3$ 3.1) Reaction of  $Ph_2P^tBu$  (1c) with  $B(C_6F_5)_3$  in a H<sub>2</sub> atmosphere in the solid state: preparation of compound <u>4c</u>

 $B(C_6F_5)_3 + PPh_2(t-Bu) \longrightarrow HPPh_2(t-Bu) / HB(C_6F_5)_3$ 1c 4c

Scheme S6. Reaction of  $Ph_2P^tBu$  (1c) with  $B(C_6F_5)_3$  in the solid state: preparation of compound 4c

A mixture of  $B(C_6F_5)_3$  (102.4 mg, 0.2 mmol) and  $Ph_2P^tBu$  (48.5 mg, 0.2 mmol) was put in a vial with a double valve adaptor<sup>a</sup> and stirred for 15 min. Then the reaction mixture was stirred in a dihydrogen atmosphere (50 bar) for 3 days. After the reaction time a part of the obtained powder (30 mg) was characterized by NMR experiments in solution(ca 95% conversion).<sup>1</sup>

The remaining solid was crystallized from dichloromethane/pentane and dried in vacuo to give compound **4c** as a white solid (90.5 mg, 0.120 mmol, yield 60 %).

<sup>1</sup>**H** NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 7.89 (m, 2H, *p*-Ph), 7.82 (m, 4H, *o*-Ph), 7.73 (m, 4H, *m*-Ph), 7.12 (d, <sup>1</sup>*J*<sub>PH</sub> = 473.7 Hz, 1H, PH), 3.67 (br 1:1:1:1q, <sup>1</sup>*J*<sub>BH</sub> ~ 90.9 Hz, 1H, BH), 1.48 (d, <sup>3</sup>*J*<sub>PH</sub> = 19.1 Hz, 9H, *t*-Bu).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 148.6 (dm, <sup>1</sup>J<sub>FC</sub> ~ 235 Hz, C<sub>6</sub>F<sub>5</sub>), 138.2 (dm, <sup>1</sup>J<sub>FC</sub> ~ 245 Hz, C<sub>6</sub>F<sub>5</sub>), 136.8 (dm, <sup>1</sup>J<sub>FC</sub> ~ 250 Hz, C<sub>6</sub>F<sub>5</sub>), 125.3 (i- C<sub>6</sub>F<sub>5</sub>), 136.4 (d, <sup>4</sup>J<sub>PC</sub> = 3.0 Hz, *p*-Ph), 133.9 (d, <sup>2</sup>J<sub>PC</sub> = 9.5 Hz, *o*-Ph), 131.3 (d, <sup>3</sup>J<sub>PC</sub> = 12.4 Hz, *m*-Ph), 114.1 (d, <sup>1</sup>J<sub>PC</sub> = 78.3 Hz, *i*-Ph), 33.4 (d, <sup>1</sup>J<sub>PC</sub> = 41.5 Hz, *t*-Bu), 25.7 (d, <sup>2</sup>J<sub>PC</sub> = 2.0 Hz, *t*-Bu).

<sup>11</sup>**B** NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -25.2 (d, <sup>1</sup>*J*<sub>BH</sub> ~ 91 Hz).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta = -25.2$  (v<sub>1/2</sub> ~ 40 Hz).

<sup>19</sup>**F** NMR (470 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta = -133.9$  (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>), -164.5 (t,

 ${}^{3}J_{\text{FF}} = 20.2 \text{ Hz}, 1\text{F}, p\text{-}C_{6}\text{F}_{5}), -167.5 \text{ (m, 2F, }m\text{-}C_{6}\text{F}_{5}), [\Delta\delta^{19}\text{F}_{\text{m,p}} = 3.0].$ 

<sup>31</sup>**P** NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 31.4 (br d, <sup>1</sup>*J*<sub>PH</sub> ~ 474 Hz).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 31.4 (v<sub>1/2</sub> ~ 2 Hz).



8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 Figure S33. <sup>1</sup>H NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the obtained powder and (2) the isolated compound 4c.



100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 Figure S35. (1,3)  ${}^{11}B{}^{1}H{}$  and (2,4)  ${}^{11}B$  NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained powder and (3,4) the isolated compound 4c.



Figure S37. (1,3)  ${}^{31}P{}^{1}H$  and (2,4)  ${}^{31}P$  NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained powder and (3,4) the isolated compound **4c**.

3.2) Reaction of Ph<sub>2</sub>P<sup>t</sup>Bu (1c) with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in solution: generation of compound 3c



Scheme S7. Reaction of  $Ph_2P^tBu$  (1c) with  $B(C_6F_5)_3$  in solution: generation of compound 3c

A solution of  $Ph_2P^tBu$  (72.7 mg, 0.3 mmol) in  $CH_2Cl_2$  (3 mL) was added to a solution of  $B(C_6F_5)_3$  (153.6 mg, 0.3 mmol) in  $CH_2Cl_2$  (3 mL). After the mixture was stirred at room temperature for 12 hours, all volatiles were removed in vacuo to give a white solid which was washed with pentane (1mL × 3) and dried in vacuo to finally give compound **3c** as a white solid (172.0 mg, 0.228 mmol, 76 %).

<sup>1</sup>**H** NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 7.86 (m, 2H, *p*-Ph), 7.71 (m, 8H, *o*,*m*-Ph), 1.60 (d, <sup>3</sup>J<sub>PH</sub> = 18.6 Hz, 9H, tBu).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 135.7 (*p*-Ph), 133.7 (d, J<sub>PC</sub> = 9.2 Hz), 130.9 (d, J<sub>PC</sub> = 12.6 Hz)(*o*,*m*-Ph), 117.7 (d, <sup>1</sup>J<sub>PC</sub> = 81.7 Hz, *i*-Ph), 37.4 (d, <sup>1</sup>J<sub>PC</sub> = 40.6 Hz, tBu), 27.8 (br m, tBu), [C<sub>6</sub>F<sub>5</sub> and C<sub>6</sub>F<sub>4</sub> not listed].

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta = -0.6$  (br d, <sup>1</sup>*J*<sub>FB</sub> ~ 68 Hz).

<sup>19</sup>**F** NMR (470 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -124.0, -128.6 (each br m, each 2F, C<sub>6</sub>F<sub>4</sub>), -135.5 (m, 4F, *o*), -161.5 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.2 Hz, 2F, *p*), -166.5 (m, 4F, *m*)(C<sub>6</sub>F<sub>5</sub>)[Δδ<sup>19</sup>F<sub>m,p</sub> = 5.0], -192.9 (br m, 1F, BF),.

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 33.3 (m).



6.0 5.5 5.0 4.5 4.0 8.0 7.5 7.0 6.5 3.5 3.0 2.5 2.0 1.5 1.0 0. 3.5 Figure S38. <sup>1</sup>H NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>) spectrum of compound 3c.





# 3.3) Reaction of $Ph_2P^tBu$ (1c) with $B(C_6F_5)_3$ in solution in a $H_2$ atmosphere: generation of a mixture of compounds 3c and 4c

A solution of  $Ph_2P^tBu$  (12.1 mg, 0.05 mmol) and  $B(C_6F_5)_3$  (25.6 mg, 0.05 mmol) in  $CD_2Cl_2$  (1 mL) was put in a vial with a double valve adaptor<sup>a</sup> and stirred for 12 hours in an H<sub>2</sub> atmosphere (50 bar). Then the reaction solution was characterized by NMR experiments.<sup>1</sup>

[Comment: the obtained NMR data showed a mixture of compounds 3c and 4c (ratio ca. 2:1 (<sup>11</sup>B)]











100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 Figure S45. (1,3,5) <sup>11</sup>B{<sup>1</sup>H}/(2,4,6) <sup>11</sup>B NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained reaction mixture, (3,4) the isolated compound **3c** and (5,6) the isolated compound **4c**.



-120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 Figure S46. <sup>19</sup>**F** NMR (470 MHz, 299K, dichloromethane- $d_2$ ) spectra of (1) the obtained reaction mixture ((the signals marked ? are likely due to subsequent BH vs BF exchange), (2) the isolated compound **3c** and (3) the isolated compound **4c**.



34 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 Figure S47. (1,3,5) <sup>31</sup>P{<sup>1</sup>H}/(2,4,6) <sup>31</sup>P NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained reaction mixture, (3,4) the isolated compound **3c** and (5,6) the isolated compound **4c** 

<u>4) Reactions of PCy<sub>3</sub> (1a) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with SO<sub>2</sub></u> <u>4.1) Reaction of PCy<sub>3</sub> (1a) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with SO<sub>2</sub> in the solid state: preparation of compound 5</u>



Scheme S8. Reaction of PCy<sub>3</sub> (1a) and  $B(C_6F_5)_3$  with SO<sub>2</sub> in the solid state: preparation of compound 5

In a Schlenk flask  $B(C_6F_5)_3$  (102.4 mg, 0.2 mmol) and  $PCy_3$  (56.1 mg, 0.2 mmol) were mixed and stirred for 15 min. Then the mixture was exposed to SO<sub>2</sub> (1.5 bar) and stirred for 4 hours. After the reaction time the obtained powder was characterized by NMR experiments in solution and in the solid state.

The obtained NMR data of the obtained powder in solution (dichloromethane- $d_2$ ) were consistent to those given for the isolated compound 5 (see below).

<u>4.2) Reaction of PCy<sub>3</sub> (1a) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with SO<sub>2</sub> in the solid state: isolation of compound 5</u>

In a Schlenk flask  $B(C_6F_5)_3$  (102.4 mg, 0.2 mmol) and  $PCy_3$  (56.1 mg, 0.2 mmol) were mixed and stirred for 15 min. Then the mixture was exposed to  $SO_2$  (1.5 bar) and stirred for 16 hours. After the  $SO_2$  gas was removed in vacuo, the obtained pale yellow solid was crystallized from dichloromethane/pentane and dried in vacuo to give compound **5** (143.9 mg, 0.168 mmol, 84 %). The obtained crystals were suitable for the X-ray crystal structure analysis.

**X-ray crystal structure analysis of compound 5:** formula C<sub>36</sub>H<sub>33</sub>BF<sub>15</sub>O<sub>2</sub>PS, M = 856.46, colourless crystal, 0.23 x 0.20 x 0.05 mm, a = 10.9369(2), b = 12.6020(2), c = 15.7611(4) Å,  $\alpha = 90.384(1)$ ,  $\beta = 97.992(1)$ ,  $\gamma = 111.759(2)^{\circ}$ , V = 1993.9(1) Å<sup>3</sup>,  $\rho_{calc} = 1.427$  gcm<sup>-3</sup>,  $\mu = 0.223$  mm<sup>-1</sup>, empirical absorption correction (0.950  $\leq T \leq 0.988$ ), Z = 2, triclinic, space group  $P_1$  (No. 2),  $\lambda = 0.71073$  Å, T = 223(2) K,  $\omega$  and  $\varphi$  scans, 18732 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), 6810 independent ( $R_{int} = 0.040$ ) and 5755 observed reflections [ $I > 2\sigma(I)$ ], 505 refined parameters, R = 0.049,  $wR^2 = 0.117$ , max. (min.) residual electron density 0.35 (-0.39) e.Å<sup>-3</sup>, hydrogen atoms were calculated and refined as riding atoms.



Figure S48. X-ray crystal structure analysis of compound 5.

<sup>1</sup>**H** NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta = 2.84$  (m, 1H, CH<sup>Cy</sup>), 2.16, 2.08, 1.89/1.37, 1.86/1.32, 1.78/1.30, 1.64, 1.62 (each br m, each 1H, CH<sub>2</sub><sup>Cy</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = 148.3 (dm, <sup>1</sup>J<sub>FC</sub> ~ 240 Hz, C<sub>6</sub>F<sub>5</sub>), 140.1 (dm, <sup>1</sup>J<sub>FC</sub> ~ 250 Hz, C<sub>6</sub>F<sub>5</sub>), 137.3 (dm, <sup>1</sup>J<sub>FC</sub> ~ 245 Hz, C<sub>6</sub>F<sub>5</sub>), 119.4 (br, i-C<sub>6</sub>F<sub>5</sub>), 32.2 (d, <sup>1</sup>J<sub>PC</sub> = 17.4 Hz, CH<sup>Cy</sup>), 27.70 (d, <sup>2</sup>J<sub>PC</sub> = 2.8 Hz)<sup>t</sup>, 27.65 (d, <sup>2</sup>J<sub>PC</sub> = 2.0 Hz)<sup>t</sup>, 27.1 (d, J<sub>PC</sub> = 11.2 Hz), 26.9 (d, J<sub>PC</sub> = 11.2 Hz), 25.7 (d, J<sub>PC</sub> = 1.5 Hz)(CH<sub>2</sub><sup>Cy</sup>), [<sup>t</sup> tentatively assigned]

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -0.3 (v<sub>1/2</sub> ~ 250 Hz).

<sup>19</sup>**F** NMR (470 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta$  = -132.3 (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>), -159.1 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.3 Hz, 1F, *p*-C<sub>6</sub>F<sub>5</sub>), -165.5 (m, 2F, *m*-C<sub>6</sub>F<sub>5</sub>), [Δδ<sup>19</sup>F<sub>m,p</sub> = 6.4].

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>)  $\delta = 50.0 (v_{1/2} \sim 10 \text{ Hz}).$ 



7.5 7.0 6.5 6.0 4.0 5.5 5.0 4.5 3.5 3.0 2.5 2.0 1.5 0.5 .0 1.0 Figure S49. <sup>1</sup>H NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the obtained powder (see experiment 4.1) and (2) the isolated compound 5 (see experiment 4.2).



<sup>100</sup> 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 Figure S51. (1,3)  ${}^{11}B{}^{1}H{}^{1}$  and (2,4)  ${}^{11}B$  NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1,2) the obtained powder (see experiment 4.1) and (3,4) the isolated compound **5** (see experiment 4.2).



130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 Figure S53.  ${}^{31}P{}^{1}H$  NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the obtained powder (see experiment 4.1) and (2) the isolated compound **5** (see experiment 4.2).

# <u>4.3) Reaction of PCy<sub>3</sub> (1a) and $B(C_6F_5)_3$ with SO<sub>2</sub> in solution: generation of compound 3a</u>

A solution of  $B(C_6F_5)_3$  (51.2 mg, 0.1 mmol) and  $PCy_3$  (28.0 mg, 0.1 mmol) in  $CD_2Cl_2$  (1 mL) was exposed to  $SO_2$  (1.5 bar) and stirred for 4 hours. Then the mixture was characterized by NMR experiments.

[Comment: the NMR data were consistent to those listed for compound **3a** (see experiment 1.3]



6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 Figure S54. <sup>1</sup>H NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the obtained reaction mixture and (2) the isolated compound **3a** (see experiment 1.3).



Figure S55. <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the obtained reaction mixture and (2) the isolated compound **3a** (see experiment 1.3).



48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 Figure S57.  ${}^{13}P{}^{1}H{}NMR$  (202 MHz, 299K, dichloromethane-d<sub>2</sub>) spectra of (1) the obtained reaction mixture and (2) the isolated compound **3a** (see experiment 1.3).

5) Reactions in perfluoromethylcyclohexane solvent

5.1) Reactions of PCy<sub>3</sub> (1a) with  $B(C_6F_5)_3$  in perfluoromethylcyclohexane in a H<sub>2</sub> atmosphere and control experiment

$$B(C_6F_5)_3 + PCy_3 \xrightarrow{C_6F_{11}CF_3} HPCy_3 / HB(C_6F_5)_3$$

$$1a \qquad 4a$$

Scheme S9. Reactions of  $PCy_3$  (1a) with  $B(C_6F_5)_3$  in perfluoromethylcyclohexane in a H<sub>2</sub> atmosphere.

In a Schlenk flask with a magnetic stirring bar,  $B(C_6F_5)_3$  (51.2 mg, 0.1 mmol) and PCy<sub>3</sub> (28.0 mg, 0.1 mmol) were suspended in perfluoromethylcyclohexane (2 mL). The reaction mixture was evacuated carefully under -78 °C (dry ice / isopropanol bath) and then stirred under H<sub>2</sub> (1.5 bar) at room temperature for 10 hours. After evaporation of all the volatiles to give a white powder, 15 mg of the powder in dichloromethane-d<sub>2</sub> (1 mL) was determined by NMR and compared with isolated compound **4a** (see experiment 1.2). The NMR shows that ca 60 % of the starting materials converted to **4a**. The white powder was also measured by solid state NMR.

<u>Control experiment</u>: In a Schlenk flask with a magnetic stirring bar,  $B(C_6F_5)_3$  (51.2 mg, 0.1 mmol) and  $PCy_3$  (28.0 mg, 0.1 mmol) were suspended in perfluoromethylcyclohexane (2 mL). The mixture was stirred in glovebox for 10 hours. White powder was obtained after evaporation of all the volatiles from this suspension. The white powder from this control experiment was also measured by NMR in solid state.



<sup>2.5</sup> 2.0 1.5 1.0 0.5 0.0 -0.5 65 5.0 4.5 4.0 3.5 3.0 6.0 5.5 Figure S58. <sup>1</sup>H NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1) and the isolated compound 4a(2)



 $_{90}^{90}$   $_{80}^{70}$   $_{70}^{60}$   $_{50}^{50}$   $_{40}^{40}$   $_{30}^{20}$   $_{20}^{10}$   $_{10}^{-10}$   $_{-20}^{-20}$   $_{-30}^{-40}$   $_{-50}^{-50}$   $_{-60}^{-70}$   $_{-80}^{-90}$   $_{-100}^{-100}$ Figure S59.  $^{11}B{^1H}$  NMR and  $^{11}B$  NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1, 2) and the isolated compound **4a** (3, 4)



-118 -122 -126 -130 -134 -138 -142 -146 -150 -154 -158 -162 -166 -170 -174 -178Figure S60. <sup>19</sup>F NMR (470 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1) and the isolated compound **4a** (2)



<sup>5</sup> 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 Figure S61.  ${}^{31}P{}^{1}H{}$  NMR and  ${}^{31}P$  NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1, 2) and the isolated compound **4a** (3, 4)

5.2) Reactions of PhPCy<sub>2</sub> (**1b**) with  $B(C_6F_5)_3$  in perfluoromethylcyclohexane in a H<sub>2</sub> atmosphere

$$B(C_6F_5)_3 + PPhCy_2 \xrightarrow{C_6F_{11}CF_3} HPPhCy_2 / HB(C_6F_5)_3$$
  
**1b 4b**

Scheme S10. Reactions of PhPCy<sub>2</sub> (1b) with  $B(C_6F_5)_3$  in perfluoromethylcyclohexane in a H<sub>2</sub> atmosphere.

In a Schlenk flask with a magnetic stirring bar,  $B(C_6F_5)_3$  (51.2 mg, 0.1 mmol) and PPhCy<sub>2</sub> (27.4 mg, 0.1 mmol) were suspended in perfluoromethylcyclohexane (2 mL). The reaction mixture was evacuated carefully under -78 °C (dry ice / isopropanol bath) and then stirred under H<sub>2</sub> (1.5 bar) at room temperature for 10 hours. After evaporation of all the volatiles to give a white powder, 15 mg of the powder in dichloromethane-d<sub>2</sub> (1 mL) was determined by NMR and compared with isolated compound **4b** (see experiment 2.1). The NMR shows that the starting materials were almost fully converted to **4b** just with little impurities (ca. 95% conversion).



<sup>80</sup> 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 Figure S63. <sup>11</sup>B{<sup>1</sup>H} NMR and <sup>11</sup>B NMR (160 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1, 2) and the isolated compound **4b** (3, 4)



<sup>110</sup> <sup>100</sup> <sup>90</sup> <sup>80</sup> <sup>70</sup> <sup>60</sup> <sup>50</sup> <sup>40</sup> <sup>30</sup> <sup>20</sup> <sup>10</sup> <sup>0</sup> <sup>-10</sup> <sup>-20</sup> <sup>-30</sup> <sup>-30</sup> Figure S65<sup>.31</sup>P{<sup>1</sup>H} NMR and <sup>31</sup>P NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1, 2) and the isolated compound **4b** (3, 4)

5.3) Reactions of PCy<sub>3</sub> (1c) with  $B(C_6F_5)_3$  in perfluoromethylcyclohexane in a H<sub>2</sub> atmosphere

$$B(C_6F_5)_3 + PPh_2(t-Bu) \xrightarrow{C_6F_{11}CF_3} HPPh_2(t-Bu) / HB(C_6F_5)_3$$
  
1c 4c

Scheme S11. Reactions of  $PCy_3$  (1c) with  $B(C_6F_5)_3$  in perfluoromethylcyclohexane in a H<sub>2</sub> atmosphere

In a Schlenk flask with a magnetic stirring bar,  $B(C_6F_5)_3$  (51.2 mg, 0.1 mmol) and PPh<sub>2</sub>(*t*-Bu) (24.2 mg, 0.1 mmol) were suspended in perfluoromethylcyclohexane (2 mL). The reaction mixture was evacuated carefully under -78 °C (dry ice / isopropanol bath) and then stirred under H<sub>2</sub> (1.5 bar) at room temperature for 10 hours. After evaporation of all the volatiles to give a white powder, 15 mg of the powder in dichloromethane-d<sub>2</sub> (1 mL) was determined by NMR and compared with isolated compound **4c** (see experiment 3.1). The NMR shows that the starting materials were almost fully converted to **4c** just with little impurities (ca. 98% conversion).



 $10^{-0}$  8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 Figure S66. <sup>1</sup>H NMR (500 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1) and the isolated compound **4c** (2)







 $^{-124}$   $^{-128}$   $^{-132}$   $^{-136}$   $^{-140}$   $^{-144}$   $^{-148}$   $^{-152}$   $^{-156}$   $^{-160}$   $^{-164}$   $^{-168}$   $^{-172}$   $^{-176}$   $^{-180}$   $^{-184}$ Figure S68. <sup>19</sup>F NMR (470 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1) and the isolated compound **4c** (2)



<sup>30</sup> <sup>120</sup> <sup>110</sup> <sup>100</sup> <sup>90</sup> <sup>80</sup> <sup>70</sup> <sup>60</sup> <sup>50</sup> <sup>40</sup> <sup>30</sup> <sup>20</sup> <sup>10</sup> <sup>0</sup> <sup>-10</sup> <sup>-20</sup> <sup>-30</sup> <sup>-40</sup> <sup>-50</sup> <sup>-50</sup> Figure S69. <sup>31</sup>P{<sup>1</sup>H} NMR and <sup>31</sup>P NMR (202 MHz, 299K, dichloromethane-d<sub>2</sub>) of the obtained powder (1, 2) and the isolated compound 4c (3, 4)

6) Reduction of an imine by compound 4a



Scheme S12. Reduction of an imine by compound **4a**.

Compound **4a** (23.8 mg, 0.03 mmol) and imine **6** (6.3 mg, 0.03 mmol) were mixed in dichloromethane- $d_2$  (1 mL). The solution was heated in a sealed *J*-Young tube at 70 °C for 24 hours and then measured by NMR. The NMR analysis shows that the conversion of the reaction is ca. 86%.



### Supplementary Information (Part 2. Solid-State NMR)

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Corresponding line shape simulations for the <sup>11</sup>B{<sup>1</sup>H} MAS and <sup>31</sup>P{<sup>1</sup>H} CPMAS NMR spectra of the hydrogenation sample and the control mixture sample (from experiment 1.1) are shown in Figure S71. Solid-state NMR characterization was carried out also for the analogous reaction in suspension (hydrogenation sample and control mixture sample: see experiment 5.1). Both reaction types yield the same reaction products (Figure S72). In suspension, the investigated product shows a higher amount of substitution product in proportion to the hydrogenation product.

The <sup>1</sup>H{<sup>11</sup>B} REAPDOR experiment in Figure S73 confirms the B-H bond near 4 ppm which was also proven by <sup>1</sup>H MAS and <sup>11</sup>B{<sup>1</sup>H} HETCOR. <sup>11</sup>B{<sup>31</sup>P} REDOR and <sup>31</sup>P{<sup>11</sup>B} CP-REAPDOR experiments (Figure S74 and Figure S75, respectively) show an insignificant dephasing effect. REDOR reveals a B-P distance of at least 5.5 Å. These experiments confirm the presence of isolated ions which was already shown by comparison of <sup>1</sup>H MAS NMR spectra and DFT calculations.



Figure S71. <sup>11</sup>B{<sup>1</sup>H} MAS (left, top) and <sup>31</sup>P{<sup>1</sup>H} CPMAS NMR spectra (right, top) of the hydrogenation sample (from experiment 1.1) measured at 7.05 T with a MAS frequency of 12.0 kHz. Line shape simulations (lower traces) result in  $\delta_{iso}(^{11}B) = -24.9$  ppm,  $C_Q = 0.99$  MHz,  $\eta_Q = 0.08$  and  $\delta_{iso}(^{31}P) = 30.1$  ppm. A minor unidentified side product is labelled by +.



Figure S72. <sup>11</sup>B{<sup>1</sup>H} MAS (left) and <sup>31</sup>P{<sup>1</sup>H} CPMAS NMR spectra (right) of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/PCy<sub>3</sub> control mixture sample (grey trace) and the hydrogenation sample (black trace, the reaction with H<sub>2</sub>). The upper traces show the spectra for the reaction in the solid state, the lower ones belong to the reaction in suspension. A minor unidentified compound is labelled by +. (solid state see experiment 1.1, suspension in perfluoromethylcyclohexane see experiment 5.1).



Figure S73. <sup>1</sup>H{<sup>11</sup>B} REAPDOR spectrum (black) and <sup>1</sup>H Spin Echo (red) of the hydrogenation sample (from experiment 1.1) measured at 11.74 T with a MAS frequency of 29.8 kHz. The difference spectrum (blue) reveals the boron bonded hydrogen species at  $\delta_{iso}(^{1}\text{H}) = 3.7$  ppm.



Figure S74. <sup>11</sup>B{<sup>31</sup>P} REDOR of the hydrogenation sample (from experiment 1.1) measured at 7.05 T with a MAS frequency of 12.0 kHz and SIMPSON simulation for a boron-phosphorus distance of 5.5 Å.



Figure S75. <sup>31</sup>P{<sup>11</sup>B} CP-REAPDOR of the hydrogenation sample (from experiment 1.1) measured at 7.05 T with a MAS frequency of 12.0 kHz.

The substitution product (compound **3a** from experiment 1.3) and the solid-state  $SO_2$  adduct (sample from experiment 4.1) were also characterized by solid-state NMR. Figures S76 to S79 summarize the solid state NMR characterization of compound **3a**, whereas Figures S80-84 show the characterization of the SO<sub>2</sub> adduct sample from experiment 4.1.



Figure S76. <sup>11</sup>B{<sup>1</sup>H} MAS NMR spectrum (top) of the substitution product (compound **3a** from experiment 1.3) measured at 7.05 T (left) and at 11.7 T (right) with a MAS frequency of 12.0 kHz. Line shape simulation (lower traces) results in  $\delta_{iso}(^{11}B) = -0.6$  ppm,  $C_Q = 0.93$  MHz and  $\eta_Q = 0.54$  and  $\delta_{iso}(^{11}B) = -0.5$  ppm,  $C_Q = 1.03$  MHz and  $\eta_Q = 0.47$ , respectively.



Figure S77. <sup>31</sup>P{<sup>1</sup>H} CPMAS NMR spectrum (top) of the substitution product (compound **3a** from experiment 1.3) measured at 7.05 T (left) with a MAS frequency of 12.0 kHz. Line shape simulation (lower traces) was done by using three signal components at  $\delta_{iso}(^{31}P) = 43.3$  ppm, 41.2 ppm and 38.0 ppm. Three phosphorus species were also verified by a  $^{31}P{^1H}$  CPMAS NMR spectrum at 11.74 T (right).



Figure S78. <sup>11</sup>B{<sup>31</sup>P} REDOR data of the substitution product (compound **3a** from experiment 1.3) measured at 7.05 T with a MAS frequency of 12.5 kHz. The experimental data are compared with SIMPSON simulations for different assumed P—B distances. The simulation most consistent with the experimental data suggests a boron-phosphorus distance of 5.4 Å. Included is also a parabolic fit, following the approach<sup>4</sup> resulting in a second moment value of  $M_2 = 0.74 \cdot 10^{-5} \text{ rad}^2/\text{s}^2$  from the parabolic fit (black curve). This approach yields a boron-phosphorus distance of 5.4 Å for an assumed two-spin interaction.



Figure S79.  ${}^{31}P{}^{11}B$  CP-REAPDOR of the substitution product (compound **3a** from experiment 1.3) measured at 7.05 T with a MAS frequency of 10.0 kHz. Included are SIMPSON simulation for different assumed B--P distances. The simulation most consistent with the experimental data is obtained for a boron-phosphorus distance of 5.0 Å and the fit to the analytical expression<sup>5</sup> given in results in 4.9 Å.



Figure S80. <sup>11</sup>B{<sup>1</sup>H} MAS NMR spectrum ( top) of the SO<sub>2</sub> adduct sample (sample from experiment 4.1) measured at 7.05 T (left) and 11.7 T (right) with a MAS frequency of 12.0 kHz. Line shape simulation (lower traces) results in  $\delta_{iso}(^{11}B) = -0.6$  ppm,  $C_Q = 1.54$  MHz and  $\eta_Q = 0.15$ . The spectrum shows a weak overlapping component arising from a second and a small third species which could be resolved by <sup>11</sup>B{<sup>1</sup>H} MQMAS.



Figure S81. <sup>11</sup>B{<sup>1</sup>H} MQMAS spectrum of the SO<sub>2</sub> adduct sample (sample from experiment 4.1) measured at 11.7 T with a MAS frequency of 12.0 kHz. The main species is located at an isotropic chemical shift of  $\delta_{iso}^{(11}B) = -0.6$  ppm and has a second order quadrupolar effect of 1.61 MHz which agrees with  $C_Q = 1.54$  MHz and  $\eta_Q = 0.15$  from the <sup>11</sup>B{<sup>1</sup>H} MAS spectrum. All results were used for line shape simulation of <sup>11</sup>B{<sup>1</sup>H} MAS spectra.



Figure S82. <sup>31</sup>P{<sup>1</sup>H} CPMAS NMR spectrum (top) of the SO<sub>2</sub> adduct sample (sample from experiment 4.1) measured at 7.05 T with a MAS frequency of 12.0 kHz. Line shape simulation (lower trace) results in  $\delta_{iso}(^{31}P) = 51.5$  ppm. Minor side products are labelled by +.



Figure S83. <sup>11</sup>B{<sup>31</sup>P} REDOR of the SO<sub>2</sub> adduct sample (sample from experiment 4.1) measured at 7.05 T with a MAS frequency of 12.5 kHz. The experimental data are compared with SIMPSON simulations for different assumed P—B distances. The simulation most consistent with the experimental data suggests a boron-phosphorus distance of 4.5 Å (blue curve). Included is also a parabolic fit, following the approach<sup>4</sup> resulting in a second moment value  $M_2 = 2.04 \cdot 10^{-5} \text{ rad}^2/\text{s}^2$  which yields a boron-phosphorus distance of 4.6 Å, assuming a two-spin interaction.



Figure S84. <sup>31</sup>P{<sup>11</sup>B} CP-REAPDOR of the SO<sub>2</sub> adduct sample (sample from experiment 4.1) measured at 7.05 T with a MAS frequency of 10.0 kHz. Included are SIMPSON simulation for different assumed B--P distances. The simulation most consistent with the experimental data is obtained for a boron-phosphorus distance of 4.5 Å and the fit by the analytical approach<sup>5</sup>.

#### **Experimental Section**

<sup>11</sup>B{<sup>1</sup>H} MAS and <sup>31</sup>P{<sup>1</sup>H} CPMAS NMR spectra were recorded at 7.05 T using a Bruker Avance III 300 spectrometer equipped with a 4 mm MAS-NMR probe, which was operated at a MAS frequency of 12.0 kHz and a nutation frequency of 69.4 kHz.  ${}^{11}B{}^{31}P{}$ rotational echo double resonance (REDOR) were conducted with the standard sequence of Schaefer and Gullion,<sup>6</sup> at the spinning frequency of 12.0 kHz, using 180° recoupling pulses of 10.0  $\mu$ s length. <sup>31</sup>P{<sup>11</sup>B} rotational echo adiabatic passage double resonance (REAPDOR) data were measured at a spinning frequency of 12.0 kHz, using a radio frequency power level corresponding to an <sup>11</sup>B nutation frequency of 33.7 kHz and a recoupling time of 1/3 of the rotor cyle. Heteronuclear correlation spectra were acquired at 11.7 T with a MAS frequency of 29.8 kHz using a Bruker DSX 500 spectrometer. These spectra were measured using the cross-polarization sequence with Hartmann-Hahn contact times of 800 µs and 7.0 ms for <sup>31</sup>P and <sup>11</sup>B, respectively. The evolution time of the <sup>1</sup>H transverse magnetization was incremented in 50 steps of 33.6 µs. <sup>1</sup>H MAS NMR experiments were performed at 20.0 T with a MAS frequency of 60.0 kHz using the EASY background suppression scheme. An empty rotor was measured additionally as described in reference.<sup>7</sup> The BCU temperature was set to 262 K to avoid any frictional heating effects of the sample. <sup>1</sup>H chemical shifts were referenced to TMS using adamantane as an internal standard (1.78 ppm). All DFT calculations were performed using the TURBOMOLE program package (version 6.3).<sup>8,9</sup> DFT calculations of <sup>1</sup>H chemical shifts were performed on a def2-TZVP<sup>[7]</sup>/B3-LYP<sup>11,12</sup> level of theory on geometries obtained from unconstrained geometry optimizations on a TPSS-D3<sup>13,14</sup>/def2-TZVP level. <sup>1</sup>H chemical shifts were referenced to TMS.

### **Supplementary Information (Part 3. Computational Section)**

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### **1** Computational details

We closely follow the recently established computational protocol from Ref. 36. The crystal structures were optimized with the composite HF-3c method.<sup>15</sup> The thermostatistical contributions to the Gibbs free energy in the gas phase were obtained from a harmonic oscillator approximation at a temperature of 298.15 K and for 1 atm pressure. HF-3c frequencies are scaled by 0.86 as recommended in the original publication.<sup>16</sup> The geometry optimization and frequency analysis calculations were performed by employing a developer version of the CRYSTAL14 software.<sup>17</sup> This is the ideal software choice for cost-efficient electronic structure calculations as it can exploit all point- and space group symmetries. Accurate electronic energies were obtained from single point calculations at the TPSS<sup>13</sup> and PBE0 level of theory on the HF-3c structures.<sup>18</sup> London dispersion interactions are included with the DFT-D3 dispersion correction in the Becke-Johnson damping scheme including the triple-dipole three-body term. <sup>14,19</sup> A projector augmented plane wave (PAW) basis set<sup>20,21</sup> was used with the energy cut-off of 800 eV. The Brillouin zone was sampled at the  $\Gamma$  point. The single point energy calculations were performed by employing the Vienna Ab initio Simulation Package, VASP 5.4.<sup>22,23</sup> All crystal lattice energies are reported per FLP molecule. The molecular structures were optimized with HF-3c and the TPSS-D3 level of theory,<sup>13,18,19</sup> in conjunction with the def2-TZVP basis set.<sup>10,24</sup> Accurate electronic energies were obtained from single point calculations at the TPSS-D3 and PW6B95-D3 level<sup>25</sup> with a Gaussian type orbital basis set of def2-TZVP quality on the HF-3c structures. The thermostatistical contributions for the molecules were obtained as noted above. The TPSS-D3 frequencies are used unscaled. The density-fitting RI-J<sup>26,27,28</sup> approach for the Coulomb integrals were used to accelerate these molecular calculations which were conducted by the Turbomole 7.0 software.<sup>29</sup> The COSMO-RS (Conductorlike Screening Model for Real Solvents) solvation model<sup>30,31</sup> was used to compute the solvation Gibbs energies by employing the gas-phase optimized structures, and with toluene as the solvent. These calculations were done with the COSMOtherm program.<sup>32</sup> The dispersion corrected density functional tight binding Hamiltonian, DFTB-D3, has been used in its third order variant with self consistent charge redistribution, damping of all hydrogen containing pair potentials by an exponent of 4.2, and 3OB Slater-Koster splines.<sup>33-35</sup> In all periodic DFTB-D3 calculations, the Brillouin zone was sampled at the  $\Gamma$  point. The Born-Oppenheimer molecular dynamics (BO-MD) simulations were performed in the NVT ensemble in which the temperatures were controlled via Nosé-Hoover thermostat.

For more computational details see Ref.<sup>36</sup>

#### **2** Benchmark results



Scheme S13. Four studied frustrated Lewis pairs.



Figure S85. The relative energy of  $H_2$  distributed in the unit cell of FLP 1 calculated at the DFTB-D3 level of theory. The contour plot in the ac-plane of the crystal (a), and the distribution of the relative energies (b).

To understand  $H_2$  mobility in the crystals, we have computed the energies for the  $H_2$  diffusion in the unit cell of FLP **1** via single point calculations at DFTB-D3 level of theory. As shown in Figure S85, one can see that most positions in the unit cell have similar energies denoting a flat potential energy surface. It indicates that  $H_2$  should be able to move inside the bulk. In other words,  $H_2$  can homogeneously distribute in the materials without too high energy barriers. Furthermore, we performed an BO-MD simulation at the DFTB3-D3 level at 300 K for a duration of 3 ps (with a time step of 0.1 fs) to qualitatively examine the  $H_2$  mobility in the crystal structure of FLP **1**. The simulations show that a hydrogen molecule can almost freely move through the channels in the crystal structure driven by the concentration gradient.

Moreover, we have also performed a BO-MD simulation at the DFTB-D3 level of theory with a crystal mass density of ca. 1.0 g cm<sup>-3</sup> for 15 ps (at 300 K and with a time step of 1 fs) to examine the "liquid" behavior of the intermolecular FLP **4** in the solid state. The results clearly show that the FLP components, in particular, the PCy<sub>3</sub> molecules move quickly from their equilibrium positions into the contact surface thereby diffusing eventually into each other (Figure S86). Hence, Lewis acid and base

components could interact at suitable distances and form solid state FLPs eventually enabling hydrogen splitting locally at contact surfaces.



Figure S86. Snapshots of the periodic BO-MD simulation at the DFTB-D3 level of theory for FLP **4**,  $PCy_3 + B(C_6F_5)_3$ . Color legend: P yellow, B pink, C black, F green and H white.

We have examined the reaction Gibbs free energies for  $H_2$  activation by FLP 1 in the solid state at different level of theory and with different numerical parameter settings (see Table S1). The results show that the reaction Gibbs free energies are independent on the level of theories, and the difference are less than 2 kcal mol<sup>-1</sup>.

Table S1. Calculated reaction Gibbs free energies for  $H_2$  activation by FLP **1** in the solid state at different level of theory and with different numerical parameter settings. All geometries were optimized at HF-3c level, the thermostatistical contributions were calculated at HF-3c level, and the single point energy calculations were performed with the same basis set (PAW). All values are given in kcal mol<sup>-1</sup>.

	$+H_2$	$+2H_2$	$+3H_2$	$+4H_2$
TPSS-D3 <sup>a</sup>	0.5	-0.6	-0.5	1.0
TPSS-D3 <sup><math>b</math></sup>	0.9	0.0	0.4	2.2
TPSS-D3 <sup>c</sup>	0.8	0.0	0.3	2.2
TPSS-D $3^d$	0.8	-0.1	0.3	2.3
PBE0-D3 <sup>a</sup>	0.6	-0.9	-0.9	0.2

<sup>*a*</sup>  $1 \times 1 \times 1$  k points and 800 eV energy cutoff; <sup>*b*</sup>  $1 \times 1 \times 1$  k points and 900 eV energy cutoff, <sup>*c*</sup>  $2 \times 1 \times 1$  k points and 900 eV energy cutoff, <sup>*d*</sup>  $2 \times 2 \times 1$  k points and 900 eV energy cutoff. +xH<sub>2</sub> denote we added one, two, three and four hydrogen molecules per unit cell.

	$\Delta E$	$\Delta G_{\rm RRHO}$	$\Delta \delta G_{ m sol}$	$\Delta G_{\text{total}}$
Solution <sup>a</sup>	-6.2	11.5	-8.8	-3.5
Solution <sup>b</sup>	-4.7	11.5	-8.8	-2.0
Solid state <sup>c</sup>	-8.6	9.6		1.0

Table S2. Calculated reaction Gibbs energies and the individual components for the  $H_2$  activation by FLP 1 in solution and in solid state. All values are in given kcal mol<sup>-1</sup>.

<sup>a</sup>TPSS-D3/def2-TZVP//HF-3c, COSMO-RS(toluene)

<sup>b</sup>PW6B95-D3/def2-TZVP//HF-3c, COSMO-RS(toluene)

<sup>c</sup>TPSS-D3/PAW//HF-3c

The direct crystal structure of FLP **4** is experimentally not available. We started from the crystal structure of **5** by removing the SO<sub>2</sub> species and optimized the structure at HF-3c level of theory. The calculated unit cell parameters are provided in Table **S3**. We compared the single point energies between TPSS-D3/def2-TZVP and PW6B95-D3/def2-TZVP level of theory, and the results are summarized in Table **S4** and **S5**. We can see that the differences are rather small, which are less than 1 kcal mol<sup>-1</sup>.

Table S3. Calculated unit cell parameters for FLP 4.

	Unit cell parameters (Å)			
	а	b	с	density
				$(g/cm^3)$
reactant	10.29	10.34	21.28	1.18
product	10.91	10.99	20.04	1.21

Table S4. Calculated reaction Gibbs free energies and the individual components for the  $H_2$  activation by FLP **4a** in the solution and in the solid state. All values are given in kcal mol<sup>-1</sup>.

	$\Delta E$	$\Delta G_{ m RRHO}$	$\Delta \delta G_{ m sol}$	$\Delta G_{ m total}$
Solution <sup>a</sup>	-11.8	7.4	-11.0	-15.5
Solution <sup>b</sup>	-11.1	7.4	-11.0	-14.8
Solid state <sup>c</sup>	-25.1	5.4		-19.7

<sup>a</sup>TPSS-D3/def2-TZVP//HF-3c, COSMO-RS(toluene) <sup>b</sup>PW6B95-D3/def2-TZVP//HF-3c, COSMO-RS(toluene) <sup>c</sup>TPSS-D3/PAW//HF-3c

Table S5. Calculated reaction Gibbs energies and the individual components for the formation of **3a** from FLP **4a** in the solution and in the solid state. All values are given in kcal mol<sup>-1</sup>.

	$\Delta E$	$\Delta G_{ m RRHO}$	$\Delta\delta G_{ m sol}$	$\Delta G_{ m total}$
Solution <sup>a</sup>	-31.4	-4.7	-14.6	-50.7
Solution <sup>b</sup>	-32.0	-4.7	-14.6	-51.2
Solid state <sup>c</sup>	-45.4	-0.4		-45.8

<sup>a</sup>TPSS-D3/def2-TZVP//HF-3c, COSMO-RS(toluene)

<sup>b</sup>PW6B95-D3/def2-TZVP//HF-3c, COSMO-RS(toluene) <sup>c</sup>TPSS-D3/PAW//HF-3c



Figure S87. Overlays of HF-3c calculated crystal structures of  $PCy_3/B(C_6F_5)_3$  (green) and  $[HPCy_3^+][HB(C_6F_5)_3^-]$  (blue) (a), and crystal structures of  $PCy_3/B(C_6F_5)_3$  (green) and the  $S_{N2Ar}$  product **3a** (orange) (b). Hydrogen atoms except P-H and B-H are omitted for clarity.



Figure S88. The distance between P and B  $(d_{PB})$  along the MD simulations.

#### References

- 1. P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich and G. Erker, *Angew. Chem. Int. Ed.*, 2008, **47**, 7543-7546.
- 2. Y. Jiang, B. Schirmer, O. Blacque, T. Fox, S. Grimme and H. Berke, *J. Am. Chem. Soc.*, 2013, **135**, 4088-4102.
- G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei and D. W. Stephan, *Dalton Trans.*, 2007, 3407-3414.
- 4. M. Bertmer and H. Eckert, *Solid State Nucl. Magn. Reson.*, 1999, **15**, 139-152.
- 5. E. Nimerovsky and A. Goldbourt, *Phys. Chem. Chem. Phys.*, 2012, **14**, 13437-13443.
- 6. J. Schaefer, J.Magn.Reson., 2011, 213, 421-422.
- 7. C. Jaeger and F. Hemmann, *Solid State Nucl.Magn.Reson.*, 2014, **57-58**, 22-28.
- 8. R. Ahlrichs, F. Furche and C. Hättig, TURBOMOLE, version 6.3, Universität Karlsruhe, 2009.
- 9. R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, 162, 165-169.
- 10. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297-3305.
- 11. A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 12. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.
- 13. J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.
- 14. S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456-1465.
- 15. R. Sure and S. Grimme, J. Comput. Chem., 2013, 34, 1672-1685.
- 16. M. Cutini, B. Civalleri, M. Corno, R. Orlando, J. G. Brandenburg, L. Maschio and P. Ugliengo, *J.Chem.Theory Comput.*, 2016, **12**, 3340-3352.
- R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De La Pierre, P. D'Arco, Y. Noël, M. Causà, M. Rérat and B. Kirtman, *Int.J.Quantum Chem.*, 2014, **114**, 1287-1317.
- 18. C. Adamo and V. Barone, J. Chem. Phys., 1999, 110, 6158-6170.
- 19. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- 20. P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953-17979.
- 21. G. Kresse and D. Joubert, *Phys. Rev.B*, 1999, **59**, 1758-1775.
- 22. G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558-561.
- 23. G. Kresse and J. Furthmüller, *Comput.Mater.Sci.*, 1996, 6, 15-50.
- 24. F. Weigend, Phys. Chem. Chem. Phys., 2006, 8, 1057-1065.
- 25. Y. Zhao and D. G. Truhlar, J. Phys. Chem. A, 2005, 109, 5656-5667.
- 26. S. Grimme, Chem. Eur. J., 2012, 18, 9955-9964.
- 27. K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem.Phys. Lett.*, 1995, **240**, 283-290.
- 28. K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, 97, 119-124.
- 29. F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka and F. Weigend, *Wiley Interdiscip. Rev.: Comput.Mol.Sci.*, 2014, **4**, 91-100.
- 30. A. Klamt and G. Schuurmann, J. Chem. Soc., Perkin Trans. 2, 1993, 799-805.
- 31. A. Klamt, J. Phys. Chem., 1995, 99, 2224-2235.
- 32. F. Eckert and A. Klamt, COSMOlogic GmbH & Co. KG, Leverkusen, Germany, 2010.
- 33. M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai and G. Seifert, *Phys.Rev. B*, 1998, **58**, 7260-7268.
- 34. M. Gaus, A. Goez and M. Elstner, J. Chem. Theory Comput., 2013, 9, 338-354.
- 35. J. G. Brandenburg and S. Grimme, J. Phys. Chem. Lett., 2014, 5, 1785-1789.
- 36. L. Liu, J. G. Brandenburg and S. Grimme, *Philos. Trans. A Math. Phys. Eng. Sci.*, 2017, **375**, 20170006.