

Supporting Information

Small Molecule Activation by Frustrated Lewis Pairs

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1. General Considerations

1.1 General Details

Air and moisture sensitive reactions were performed on a dual-manifold vacuum/N₂ line using standard Schlenk techniques, or in a N₂ filled MBraun Unilab glovebox. Hexane, pentane, toluene and DCM were dried using a Braun SPS-800 solvent purification system. Et₂O and THF were dried at reflux over Na/benzophenone and distilled under N₂. Hexane, pentane and toluene were stored over K mirrors. THF and Et₂O were stored over activated 3 Å molecular sieves. H₂ gas (>99.95%) was obtained from Sigma Aldrich and passed directly into a dual manifold Schlenk. CO₂ gas (99.99%) was obtained from ARGO International Ltd. and connected directly into a Schlenk line. Toluene-*d*₈ (99.6%) was obtained from Cambridge Isotope Laboratories Inc., dried over K and freeze-pump-thaw degassed (x3). Benzene-*d*₆ (99%) and Chloroform-*d*₁ (99%) were obtained from Goss Scientific, dried over K and preactivated 3 Å molecular sieves respectively, freeze-pump-thaw degassed three times before being vac transferred prior to use. THF-*d*₈ was dried over CaH₂, freeze-pump-thaw degassed three times before being vac transferred prior to use, and was obtained from Sigma Aldrich. Fe powder was purchased from East Anglia chemicals; MgCO₃, Na₂S₂O₃, conc. H₂SO₄ and I_{2(s)} from Fischer Scientific; with the remaining chemicals utilised in the preparations below obtained from Sigma Aldrich. All were used as received.

1.2 Solution NMR spectroscopy

Solution NMR samples were prepared in the glovebox under N₂ atmosphere in Young's tap NMR tubes, which were subsequently filled by H₂ or CO₂ as appropriate by freeze-pump-thaw cycles (x3). ¹H, ¹³C{¹H}, ¹¹B, ¹¹B{¹H}, ¹⁹F, ³¹P and ³¹P{¹H} NMR spectra were recorded on 300 MHz Varian VX-Works spectrometers. All chemical shifts were expressed as δ, in parts per million (ppm), ¹H and ¹³C{¹H} relative to TMS (δ=0), and referenced internally to the residual proton shift in the deuterated solvent used. ¹¹B{¹H}, ¹⁹F and ³¹P{¹H} were referenced externally to BF₃·OEt₂, CFC₃ and 85% H₃PO₄ (δ=0), respectively.

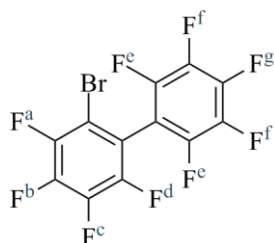
1.3 Single crystal X-ray diffraction

Crystals were mounted on MiTeGen MicroMants using perfluoropolyether oil, and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit.¹ Data collections were performed using an Enraf-Nonius FR590 KappaCCD diffractometer, utilising graphite-monochromated Mo K_α X-ray radiation (λ = 0.71073 Å). Raw frame data were collected at 150(2) K using a Nonius Kappa CCD diffractometer, reduced using DENZO-SMN² and corrected for absorption using SORTAV.³ The structure was solved using SuperFlip⁴ and refined using full matrix least-squares using CRYSTALS.^{5,6} Dihedral angles were calculated using PLATON.^{7,8}

2. Synthesis of Lewis Acids and FLP

2.1 Synthesis of: 2-bromononafluorobiphenyl

Prepared according to literature synthesis.⁹

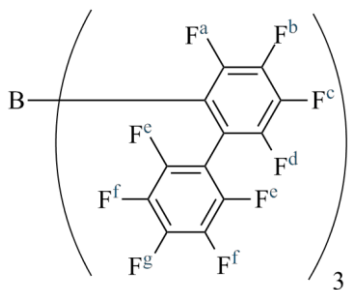


1.1 equivalents of ⁿbutyllithium (8.09 ml, 22.2 mmol, 2.5 M in hexanes) was added dropwise at $-78\text{ }^{\circ}\text{C}$ to one equivalent of bromopentafluorobenzene (10.00 g, 5.05 ml, 40.5 mmol) in diethylether (60 ml). The solution was stirred for 16 hours at room temperature, giving a cloudy yellow solution. Removal of the solvent followed by vacuum sublimation at $60\text{-}65\text{ }^{\circ}\text{C}/10^{-2}$ Torr gave 6.64 g of 2-bromononafluorobiphenyl as a white solid, yield 83%.

^{19}F NMR: δ (ppm), 282.5 MHz -126.7 (F_d , d, $^3J_{\text{F}_d\text{-F}_c} = 23.4$ Hz, 1F), -135.0 (F_a , d, $^3J_{\text{F}_a\text{-F}_b} = 22.7$ Hz, 1F), -138.7 (F_e , d, $^3J_{\text{F}_e\text{-F}_f} = 26.5$ Hz, 2F), -148.7 (F_c , td, $^3J_{\text{F}_c\text{-F}_b,d} = 22.5$ Hz, $^5J_{\text{F}_c\text{-F}_a} = 5.1$ Hz, 1F), -150.1 (F_g , tt, $^3J_{\text{F}_g\text{-F}_f} = 22.1$ Hz, $^5J_{\text{F}_c\text{-F}_e} = 3.4$ Hz 1F), -154.3 (F_b , td, $^3J_{\text{F}_b\text{-F}_a,c} = 22.3$ Hz, $^5J_{\text{F}_b\text{-F}_d} = 4.5$ Hz, 1F), -160.7 (F_f , m, 2F).

2.2 Synthesis of tris(2,2',2''-nonafluorobiphenyl)borane (PBB)

Prepared according to the literature procedure.⁹

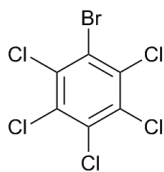


Three equivalents of ⁿbutyllithium (8.24 ml, 20.6 mmol, 2.5 M in hexane) were added dropwise at $-78\text{ }^{\circ}\text{C}$ to three equivalents of 2-bromononafluorobenzene (8.10 g, 20.6 mmol) in Et₂O (80 ml) and pentane (80 ml). The solution was stirred for 2 hours at $-78\text{ }^{\circ}\text{C}$ before one equivalent of boron trichloride (6.90 ml, 6.9 mmol, 1.0 M in heptane) was added quickly. The solution was stirred for 3 hours at $-78\text{ }^{\circ}\text{C}$ before slowly raising to room temperature to stir for an additional 64 hours. A colour change from dark green to turquoise to cloudy yellow with blue residue around the Schlenk was observed. The solution was filtered, and then the solvent removed. A vacuum sublimation at $140\text{ }^{\circ}\text{C}/10^{-2}$ Torr, followed by recrystallisation in pentane yielded 5.29 g of PBB as white crystals, at a yield of 77%.

The solution was filtered, and then the solvent removed. A vacuum sublimation at $140\text{ }^{\circ}\text{C}/10^{-2}$ Torr, followed by recrystallisation in pentane yielded 5.29 g of PBB as white crystals, at a yield of 77%.

^{19}F NMR: δ (ppm), 282.5 MHz -119.9 (F_d , s, 3F), -132.0 (F_a , s, 3F), -137.4 (F_e , s, 6F), -143.2 (F_c , td, $^3J_{\text{c-b,d}} = 19.0$ Hz, $^4J_{\text{c-a}} = 8.6$ Hz, 3F), 149.1 (F_g , t, $^3J_{\text{g-f}} = 22.8$ Hz, 3F), -150.5 (F_b , td, $^3J_{\text{b-a,c}} = 22.3$ Hz, $^5J_{\text{b-d}} = 6.0$ Hz, 3F), 160.6 (F_f , t, $^3J_{\text{f-e,g}} = 19.9$ Hz, 6F). $^{11}\text{B}\{^1\text{H}\}$ NMR: δ (ppm), 96.2 MHz 70.9 (br). ^{13}C NMR{ ^1H }: δ (ppm) 75.51 MHz 152.01 (s), 148.48 (s), 147.27 (s), 145.40 (s), 138.80 (s), 135.36 (s), 123.84 (s), 113.33 (s), 105.94 (s).

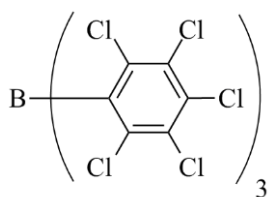
2.3 Synthesis of bromopentachlorobenzene



Prepared according to synthesis reported.¹⁰ Bromine (4.00 ml, 77.7 mmol), oleum (50 ml), I₂ (220 mg), and Fe powder (220 mg) were added to pentachlorobenzene (10.00 g, 39.9 mmol) in a round bottomed flask which was heated to 70 °C, and left to cool overnight. The resulting suspension filtered, leaving behind a grey solid that was then washed with saturated solutions of NaS₂O₃ (aq) and MgCO₃ (aq). This solid was dried overnight before being dissolved in two litres of hot hexane, filtered before being dried under roto-evap, leaving white crystals which were recrystallised from one litre of hot toluene leaving white crystalline bromopentachlorobenzene (8.41 g, 64% yield).

¹³C{¹H} NMR: δ (ppm), 75.51 MHz 134.2 (s), 133.0 (s), 132.0 (s), 123.8 (s).

2.4 Synthesis of Tris(pentachlorophenyl)borane (BAr^{Cl})



3.3 equivalents of ⁿButyllithium (5.35 ml, 13.3 mmol) were added to three equivalents of bromopentachlorobenzene (4.00 g, 12.1 mmol) in diethyl ether (140 ml) at -78 °C. The solution was stirred for 10 minutes before warming gradually to -10 °C until no more bromopentachlorobenzene was visible, and the solution was a clear orange colour. The Schlenk was cooled back down to -78 °C before one equivalent of boron trichloride was added (4.00 ml, 4.00 mmol) and the Schlenk left to gradually approach room temperature and stir for a further 16 hours. The resulting cloudy orange liquid was quenched with 0.5 ml of cold water before having solvent removed. The resulting solid was dissolved in DCM and filtered through Celite before removing the solvent again. Recrystallisation in two litres of hot toluene left 1.78 g of orange microcrystals of BAr^{Cl}, Yield 58%.

¹¹B{¹H} NMR: δ (ppm) 96.2 MHz 69.5 (br, s) ¹³C{¹H} NMR: δ (ppm), 75.51 MHz 140.5 (br, *ipso*-C₆Cl₅); 136.5 (s, *para*-C₆Cl₅); 134.8 132.6 (both s, *meta*-C₆Cl₅ and *ortho*-C₆Cl₅).

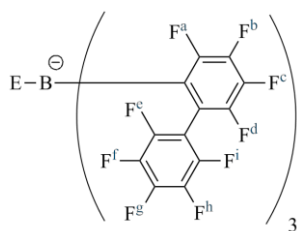
2.5 Synthesis of FLP

Table S1: Specific reactant amounts used in the preparation of PBB based FLP.

Frustrated Lewis Pair	Borane	Phosphine
PBB/P(<i>p</i> -tolyl) ₃	PBB (31.4 μmol, 30 mg)	P(<i>p</i> -tolyl) ₃ (31.4 μmol, 8.23 mg)
PBB/P(Et) ₃	PBB (31.4 μmol, 30 mg)	P(Et) ₃ (31.4 μmol, 4.62 μl)
PBB/P(^{<i>n</i>} Bu) ₃	PBB (31.4 μmol, 30 mg)	P(^{<i>n</i>} Bu) ₃ (31.4 μmol, 7.74 μl)
PBB/P(^{<i>t</i>} Bu) ₃	PBB (31.4 μmol, 30 mg)	P(^{<i>t</i>} Bu) ₃ (31.4 μmol, 6.35 mg)
PBB/P(Cy) ₃	PBB (31.4 μmol, 30 mg)	P(Cy) ₃ (31.4 μmol, 8.80 mg)

Table S2: Specific reactant amounts used in the preparation of BAr^{Cl} based FLP.

Frustrated Lewis Pair	Borane	Phosphine
BAr ^{Cl} /P(<i>p</i> -tolyl) ₃	BAr ^{Cl} (32.9 μmol, 25 mg)	P(<i>p</i> -tolyl) ₃ (32.9 μmol, 10.0 mg)
BAr ^{Cl} /P(Et) ₃	BAr ^{Cl} (32.9 μmol, 25 mg)	P(Et) ₃ (32.9 μmol, 4.85 μl)
BAr ^{Cl} /P(^{<i>n</i>} Bu) ₃	BAr ^{Cl} (32.9 μmol, 25 mg)	P(^{<i>n</i>} Bu) ₃ (32.9 μmol, 8.26 μl)
BAr ^{Cl} /P(^{<i>t</i>} Bu) ₃	BAr ^{Cl} (32.9 μmol, 25 mg)	P(^{<i>t</i>} Bu) ₃ (32.9 μmol, 6.67 μl)
BAr ^{Cl} /P(Cy) ₃	BAr ^{Cl} (32.9 μmol, 25 mg)	P(Cy) ₃ (32.9 μmol, 9.24 μl)



In the case of adducts of PBB where fluorine positions can be assigned, they are done so according to the convention.

Table S3: Reaction conditions for the hydrogenation reactions of BAr^{Cl} FLP systems.

Frustrated Lewis Pair	Time heated at 90 °C
BAr ^{Cl} /P(<i>p</i> -tolyl) ₃	60 hours at 90 °C, 24 hours at 120 °C, 48 hours at 140 °C
BAr ^{Cl} /PEt ₃	48 hours at 90 °C
BAr ^{Cl} /P ^{<i>n</i>} Bu ₃	48 hours at 90 °C
BAr ^{Cl} /P ^{<i>t</i>} Bu ₃	52 hours at 90 °C
BAr ^{Cl} /PCy ₃	40 hours at 90 °C

3. NMR Spectroscopy

3.1 Reactions using PBB

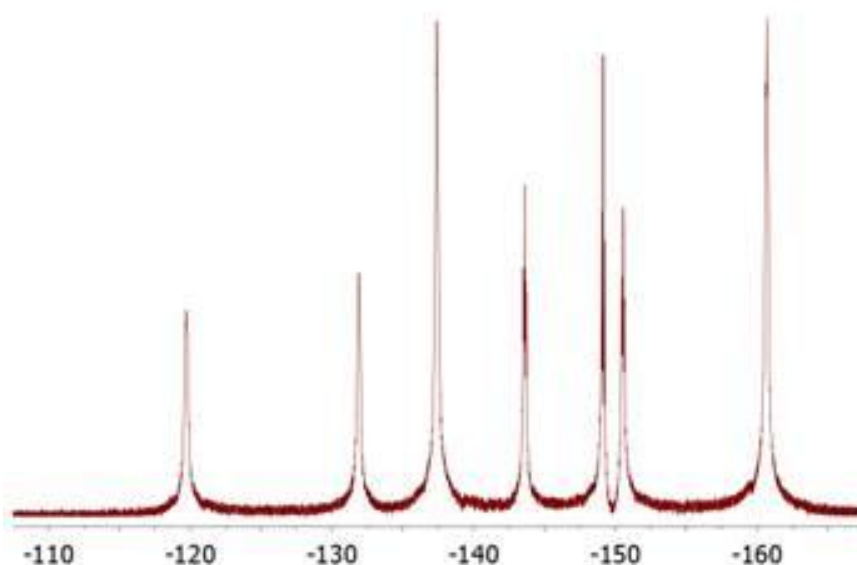


Figure S1. ^{19}F of PBB.

Table S4. Chemical shift from the reaction of PBB with phosphines.

	$\Delta\delta^{31}\text{P}\{^1\text{H}\}^{\text{a}}$ (ppm)	$^{11}\text{B}\{^1\text{H}\}$ after reaction (ppm)	Observations	Adduct / FLP formed
$\text{P}(p\text{-tolyl})_3$	+ 22.1	0.8	Forms deep red oil	Adduct
$\text{P}(\text{Et})_3$	+ 57.6	0.4	Forms orange oil	Adduct
$\text{P}(^n\text{Bu})_3$	+ 64.4	0.5	Forms dark grey oil	Adduct
$\text{P}(^t\text{Bu})_3$	0.0	70.9	Forms yellow solution	FLP
$\text{P}(\text{Cy})_3$	+ 29.8	0.2	Forms blue-green oil	Adduct

a) Where $\Delta\delta^{31}\text{P}\{^1\text{H}\} = \delta^{31}\text{P}[\text{after addition of PBB}] - \delta^{31}\text{P}[\text{free phosphine}]$.

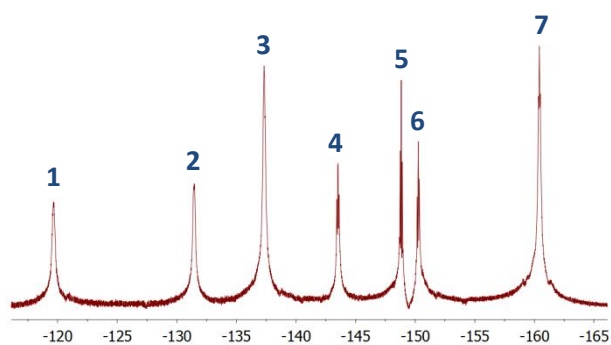


Figure S2a: ^{19}F NMR spectrum of PBB, (toluene- d_8 , 25 °C 300 Mhz).

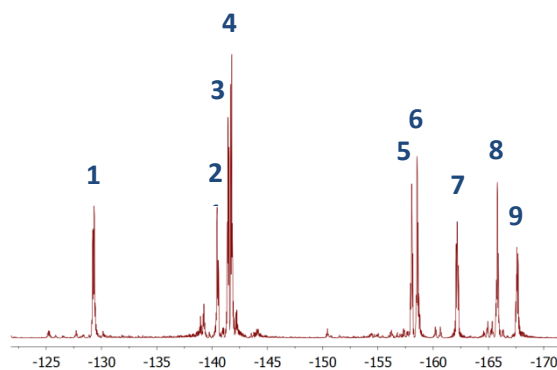


Figure S2b: ^{19}F NMR spectrum of the PBB / P(*p*-tolyl) $_3$ adduct (toluene- d_8 , 25 °C 300 Mhz).

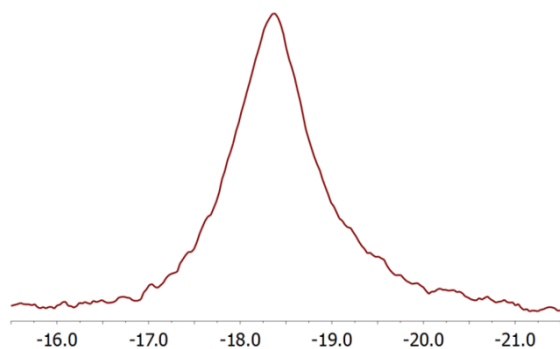


Figure S3a: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of using [PBB-H][H-P(*t*Bu) $_3$] (toluene- d_8 , 25 °C).

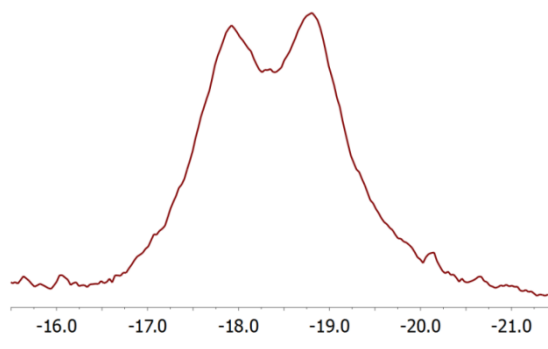


Figure S3b: ^{11}B NMR spectrum of [PBB-H][H-P(*t*Bu) $_3$] (toluene- d_8 , 25 °C).

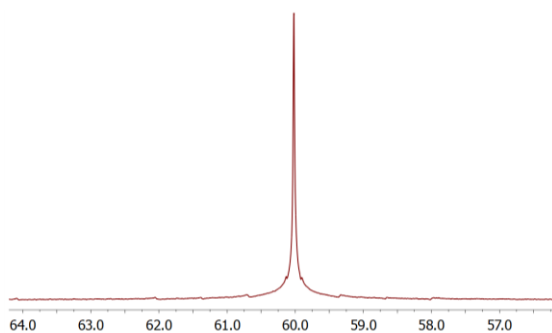


Figure S4a: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of [PBB-H][H-P(*t*Bu) $_3$] (toluene- d_8 , 25 °C).

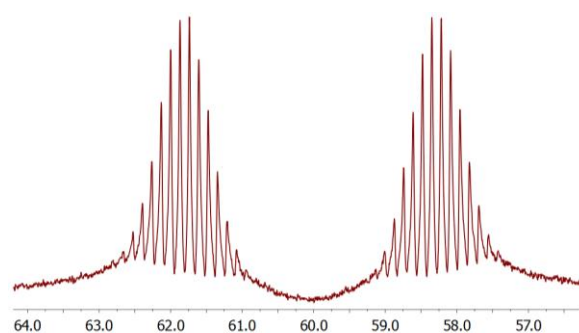


Figure S4b: Coupled ^{31}P NMR spectrum of [PBB-H][H-P(*t*Bu) $_3$] (toluene- d_8 , 25 °C).

3.2 Reactions using BAr^{Cl}

Table S5. Hydrogen splitting using R₃P/BAr^{Cl}.

	¹¹ B resonance	³¹ P resonance	Conclusion
P(<i>p</i> -tolyl) ₃	-8.37 ppm, (¹ J _{B-H} = 83.0 Hz)	Not observed	Hydride salt observed in low yield after stepwise heating up to 140 °C
P(Et) ₃	-8.43 ppm, (¹ J _{B-H} = 67.8 Hz)	Not observed	Hydride salts formed alongside thermal decomposition products
P(^{<i>n</i>} Bu) ₃	-8.54 ppm (¹ J _{B-H} = 81.8 Hz)	Not observed	Hydride salts formed alongside thermal decomposition products
P(^{<i>t</i>} Bu) ₃	-8.19 ppm (¹ J _{B-H} = 77.9 Hz)	58.84 ppm (¹ J _{P-H} = 445.7 Hz)	95 % conversion to hydride salt after 56 hours at 90 °C
P(Cy) ₃	-8.78 ppm (¹ J _{B-H} = 81.4 Hz)	32.94 ppm (¹ J _{P-H} = 475.3 Hz)	96 % conversion to hydride salt after 40 hours at 90 °C

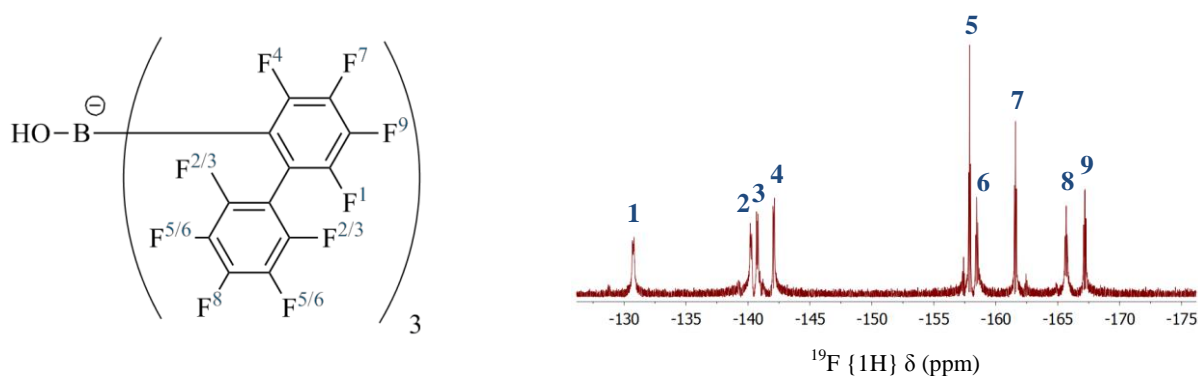


Figure S5: The ¹⁹F NMR spectrum of [PBB-OH][H-P(^{*t*}Bu)₃] (toluene-*d*₈, 25 °C).

4. X-ray crystallography

Table S6. Selected bond lengths and angles.

	Bond lengths (Å)
B-O	1.463(7)
B-C	1.642(3)
C-C between biphenyl rings	1.490(5)
H to OH (intermolecular)	5.787

	Bond angles (degrees)
C-B-C (average)	113.10(19)
Dihedral angle between biphenyl rings (average)	77.8(4)
H-P-C (average)	103.7
C-B-O	105.5(2)

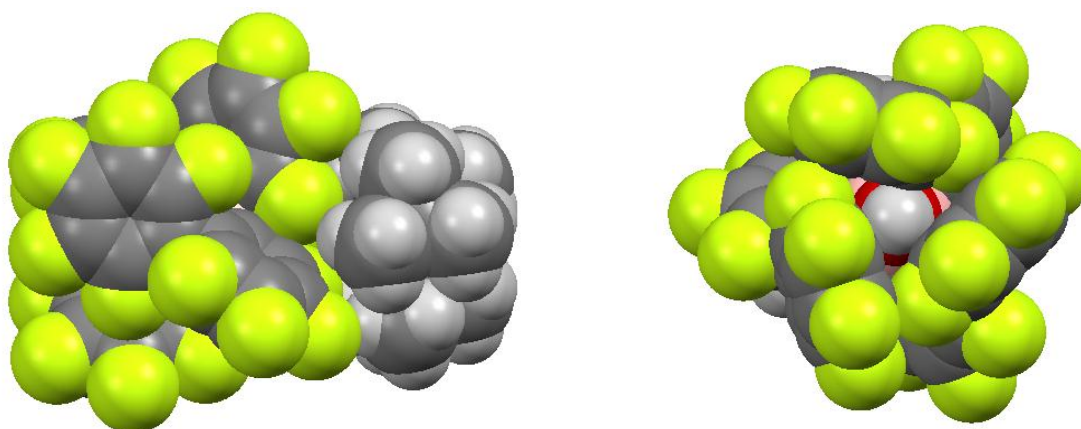


Figure S6. Space filling structure of [PBB-OH][H-P'Bu₃], fluorine (green), carbon (dark grey), hydrogen (light grey), oxygen (red) and boron (pink).

	[PBB-OH][HP(t-Bu)3]
Chemical formula	C ₄₈ H ₂₉ BF ₂₇ OP
<i>M_r</i>	1176.49
Crystal system, space group	Trigonal, <i>R</i> 3
Temperature (K)	150
<i>a</i> , <i>c</i> (Å)	16.0095 (3), 15.8189 (4)
<i>V</i> (Å ³)	3511.26 (13)
<i>Z</i>	3
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.21
Crystal size (mm)	0.35 × 0.20 × 0.16
<i>T_{min}</i> , <i>T_{max}</i>	0.82, 0.97
No. of measured, independent and observed reflections	19434, 3541, 2478 { <i>I</i> > 2.0σ(<i>I</i>)}
<i>R_{int}</i>	0.065
(sin θ/λ) _{max} (Å ⁻¹)	0.649
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.042, 0.106, 0.97
No. of reflections	3541
No. of parameters	241
No. of restraints	7
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.58, -0.55

5. Formatoborate formation

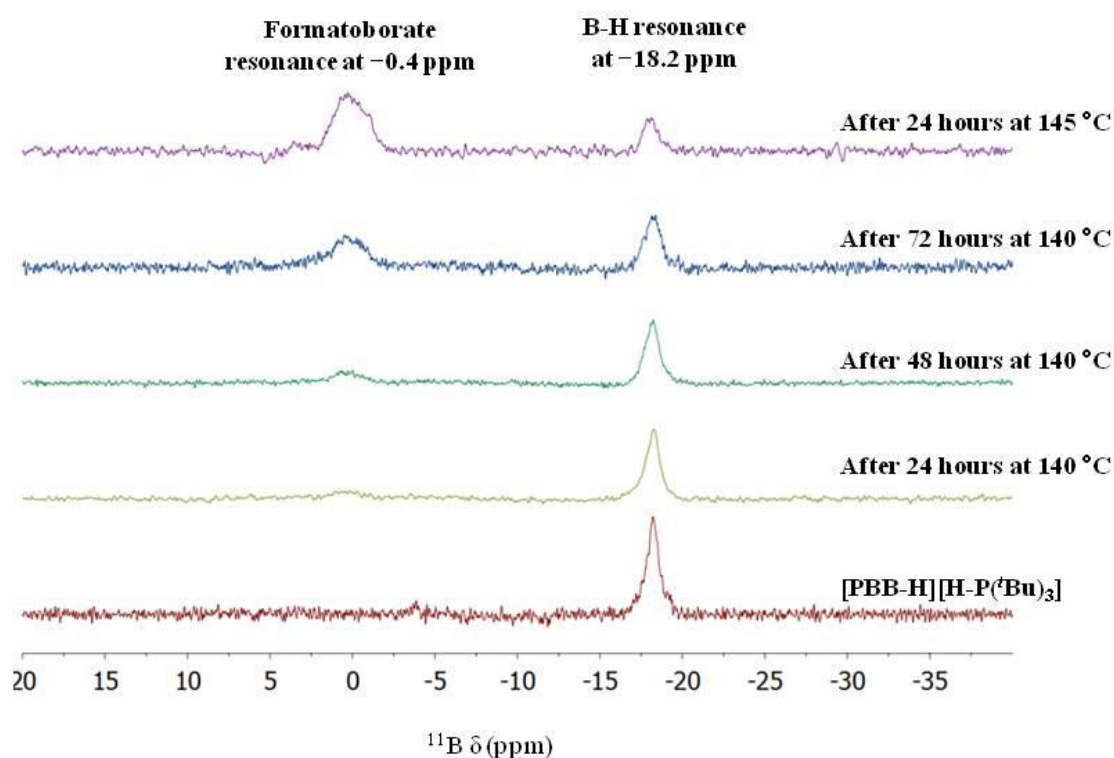


Figure S7. ^{11}B NMR spectrum of the formation of $[\text{PBB-OC(O)-H}][\text{H-P}(\text{tBu})_3]$ via CO_2 inserting into $[\text{PBB-H}][\text{H-P}(\text{tBu})_3]$, (toluene- d_8 , 25°C).

Table S7. Summary of the reactivity of $[\text{BAR}^{\text{Cl}}\text{-H}][\text{H-phosphine}]$ systems with CO_2 via route A.

	Reactivity with H_2	Thermal decomposition of Hydride?	Formatoborate observed?	Reversible loss of H_2 ?
$\text{P}(p\text{-tolyl})_3$	Hydride salt produced in low yield	No	No	No
$\text{P}(\text{Et})_3$	Hydride salt produced, along with side products	Yes	-	-
$\text{P}(\text{tBu})_3$	Hydride salt produced, along with side products	Yes	-	-
$\text{P}(\text{tBu})_3$	Hydride salt produced in 96 % yield	No	No	Yes
$\text{P}(\text{Cy})_3$	Hydride salt produced in 95% yield	No	No	No

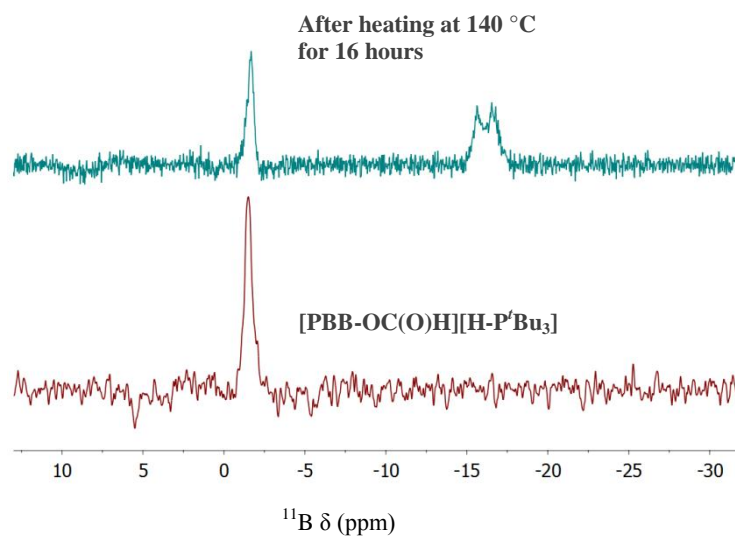


Figure S8. Formation of methoxyborate.

6. References

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