Supplementary Data for:

Stoichiometric CO$_2$ Reductions using a Bis-Borane-based Frustrated Lewis Pair†

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**Synthesis of C$_6$H$_4$(BCl$_2$)$_2$PtBu$_3$ (2):** 1,2-Bis(dichloroboryl)benzene (1) (24 mg, 0.10 mmol) was dissolved in bromobenzene (2 mL). tert-Butyl-Phosphine (20 mg, 0.10 mmol, 1.0 eq) was added and the reaction mixture was allowed to stir for 15 min at ambient temperature. The reaction mixture was cooled to 260K overnight. A white precipitate formed, was collected, washed with pentane (2 x 3 mL), and dried *in vacuo*. Yield: 37 mg, 84%.

A solution of tBu$_3$P (24 mg, 0.117 mmol) in C$_6$H$_6$ (2 mL) was stirred and THF was added drop wise (0.25 mL) giving a cloudy white suspension. CH$_2$Cl$_2$ was added to the mixture which was then stirred for an additional 12 h. Pentane was added to precipitate a white solid that was collected by filtration. The solid was washed 3 times with pentane and recrystallized from a layered mixture of DCM and pentane. The product was obtained as colorless needles in 97% yield (64 mg, 0.113 mmol).

**Synthesis of C$_6$H$_4$(BCl$_2$)$_2$O(CH$_2$)$_2$PtBu$_3$ (3):** A solution of tBu$_3$P (24 mg, 0.117 mmol) in C$_6$H$_6$ (2 mL) added to a neat sample of (1) (34 mg, 0.117 mmol) in a 4 dram scintillation vial. The clear colorless solution was stirred and THF was added drop wise (0.25 mL) giving a cloudy white suspension. CH$_2$Cl$_2$ was added to the mixture which was then stirred for an additional 12 h. The reaction mixture was subjected to 3 freeze-pump-thaw cycles and backfilled with 1.0 bar CO$_2$. The reaction mixture was allowed to stand at room temperature overnight, during which time a
The aqueous layer was suspended in pentane (2 mL), and dried in vacuo. Yield 157 mg, 77%. C_{19}H_{34}B_{2}Cl_{2}O_{2}P, M: 485.86 g/mol

Elemental Analysis: calculated for C_{19}H_{34}B_{2}Cl_{2}O_{2}P+1/6(C_{6}H_{6}): C 48.33; H 6.50; Found: C 48.28; H 6.46. \(^1\)H NMR (400 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 7.36 \) (dd, \(\text{J}_{\text{HH}}=2.9 \text{ Hz}, 3.4 \text{ Hz}, 2 \text{H} \)), 7.18 (dd, \(\text{J}_{\text{HH}}=2.9 \text{ Hz}, 3.4 \text{ Hz}, 2 \text{H} \)), 1.58 (d, \(\text{J}_{\text{HH}}=14.8 \text{ Hz}, 9 \text{ H} \)) ppm. \(^{13}\)C NMR (100 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 156.3 \) (d, \(\text{J}_{\text{BC}}=94.6 \text{ Hz}, \text{CO}_{2} \)), 129.6 (CH), 127.9 (CH), 41.7 (d, \(\text{J}_{\text{BC}}=19.8 \text{ Hz}, \text{PC(CH}_{2})_{3} \)), 30.7 (CH_{2}) ppm. Quaternary carbons of C_{6}H_{2}B_{2} ring were not observed. \(^{31}\)P\(^{1}\)H NMR (161 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 48.4 \) (s ppm). \(^{11}\)B NMR (128 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 18.0 \) ppm. IR: 1718.96 cm\(^{-1} \) (CO_{2})

**Synthesis of [B(C_{6}F_{5})]_{2}[C_{6}H_{2}Me_{2}C_{3}H_{3}] (5):** In a thick walled Young reaction flask equipped with a Teflon cap, bis-(pentfluorophenyl)borane (100 mg, 0.29 mmol) was suspended in pentane (2 mL). Norbornylene (27 mg, 0.29 mmol), dissolved in pentane (2 mL) was added drop wise. The reaction mixture was allowed to stir for 10 minutes. 2,2,6,6-Tetramethylpiperidin (41 mg, 0.29 mmol), dissolved in pentane (2 mL) was added and the reaction mixture was allowed to stir for 10 minutes. The solution was subjected to 3 freeze-pump-thaw cycles and backfilled with 1.0 bar H_{2} at 77 K (approx. 4 bar at 293 K). The reaction mixture was allowed to stir overnight. The white precipitate was separated from the solution, washed with pentane (2 x 3 mL) and dried in vacuo. Yield: 91 mg, 54%. C_{28}H_{32}B_{10}N, M: 583.36 g/mol. Elemental Analysis, calculated for C_{28}H_{32}B_{10}N: C 57.65; H 5.53; N 2.40, found: C 57.54; H 6.16; N 2.82. \(^{1}\)H NMR (400 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 5.52 \) (br, 2H, NH_{2}), 1.55 (s, 12H, CH_{2}), 2.10 (s, 1H), 1.87 (m, 3H), 1.80 (m, 4H), 1.50, (br, 2H), 1.30 (m, 4H), 1.19, (m, 1H), 1.09 (br, 1H), 0.98 (m, 1H) ppm. \(^{13}\)C NMR (100 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 58.4 \) (NC(CH_{3})_{3}), 40.1 (BCH), 37.7, 37.2, 35.8 (NC(CH_{3})_{2}CH_{2}), 34.8, 34.7, 34.1, 29.0, 27.8 (CH_{3}), 16.0 (NC(CH_{3})_{2}CH_{2}CH_{2}) ppm, Carbons of C_{6}F_{6} ring were not observed. \(^{19}\)F NMR (376 MHz, CD_{2}Cl_{2}, 300K): \(\delta = -132.2 \) (d, \(\text{J}_{\text{FF}}=20.6 \text{ Hz}, 4 \text{F} \)), \(-164.5 \) (dd, \(\text{J}_{\text{FF}}=20.6 \text{ Hz}, 19.5 \text{ Hz} \)), \(-166.5 \) (m, 4F, m-C_{6}F_{5}) ppm, \(^{11}\)B NMR (128 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 17.2 \) (d, \(\text{J}_{\text{BH}}=81.0 \text{ Hz} \)) ppm.

**Reductions:** All experiments to reduce the activated CO_{2} were performed with in situ formed Ph(BCl_{2})_{2}CO_{2}PtBu_{3} in J-Young NMR tubes in an analogous fashion to the following procedure.

1,2-Bis(dichloroboryl)benzene (12 mg, 0.05 mmol) and tert-butyl-phosphine (10 mg, 0.05 mmol, 1.0 eq.) were dissolved in 0.75 mL CD_{2}Cl_{2}. The solution was subjected to 3 freeze-pump-thaw cycles and backfilled with 1.0 bar \(^{13}\)CO_{2}. After 15 min, the formation of Ph(BCl_{2})_{2}CO_{2}PtBu_{3} was verified by NMR measurements. After addition of 3.0 equivalents of the reducing agent (Me_{2}NHBH_{3}, [B(C_{6}F_{5})_{3}]HTMP), or [NorbornylH[Bi(C_{6}F_{5})_{2}][HTMP]], the mixture was allowed to react for various reaction times at room temperature. D_{2}O (0.75 mL) was injected into the NMR tube. After 5 min, the aqueous layer was separated and injected into a NMR tube containing a pre-weight amount of 1,4-dioxane. Successful reduction to MeOD was verified by NMR spectroscopy: \(^{1}\)H NMR (400 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 3.22 \) (d, \(\text{J}_{\text{CS}}=142Hz \)) ppm. \(^{13}\)C NMR (100 MHz, CD_{2}Cl_{2}, 300K): \(\delta = 48.8 \) (q, \(\text{J}_{\text{CS}}=142Hz \)) ppm.

The yield was determined by \(^{1}\)H NMR spectroscopy using the 1,4-dioxane as internal standard.
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<thead>
<tr>
<th>Reducing agent</th>
<th>Reaction time at rt</th>
<th>Yield (based on PtBu$_3$)</th>
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<tbody>
<tr>
<td>Me$_2$NHBH$_3$</td>
<td>15 min</td>
<td>34%</td>
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<tr>
<td>[B(C$_6$F$_5$)$_3$][HTMP]</td>
<td>24 h</td>
<td>15%</td>
</tr>
<tr>
<td>[NorbonylHB(C$_6$F$_5$)$_2$][HTMP]</td>
<td>60 min</td>
<td>57%</td>
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