Supplementary Data for:

Stoichiometric CO_2 Reductions using a *Bis*-Borane-based Frustrated Lewis Pair[†]

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1,2-Bis(dichloroboryl)benzene (1): This was prepared as reported in D. Kaufmann, *Chem. Ber.* **1987**, *120*, 901-905. and V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins, T. B. Marder, *J. Am. Chem. Soc.*, **1999**, *121*, 3244-3245.

Synthesis of $C_6H_4(BCl_2)_2PtBu_3$ (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%. $C_{18}H_{31}B_2Cl_4P$ M: 441.85 g/mol Elemental Analysis: calculated for $C_{18}H_{31}B_2Cl_4P$ C 48.93; H 7.07; found: C 49.03; H 7.08. ^1H NMR (400 MHz, CD_2Cl_2, 300K): δ = 7.55 (br, 2 H), 7.74 (br, 2 H), 1.72 (br, 9 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 300K): δ = 37.3 (d, $^1J_{PC}$=27.1 Hz, P*C*$(CH_3)_3$), 30.3 (CH_3) ppm. Carbons of the $C_6H_4B_2$ ring were not observed. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 300K): δ = 28.5 (br) ppm, ^{11}B NMR (128 MHz, CD_2Cl_2, 300K): δ = 22.3 (br), 12.9 (br) ppm.

Synthesis of $C_6H_4(BCl_2)_2O(CH_2)_4PtBu_3$ (3): A solution of tBu_3P (24 mg, 0.117 mmol) in C_6H_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_2Cl_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). ^1H NMR (400 MHz, CD_2Cl_2, δ ppm) 7.34 (d of d, 2H, $^3J_{HH}$ 5.38 Hz, $^4J_{HH}$ 2.20 Hz Ar-CH), 7.19 (d of d, 2H, $^3J_{HH}$ 5.38 Hz, $^4J_{HH}$ 2.20 Hz Ar-CH), 4.70 (bt, 2H, $^3J_{HH}$ 5.38 Hz, O-C*H*$_2$), 2.29 (m, 6H, CH_2), 1.57 (d, 27H, $^3J_{HP}$ 13.9 Hz, C(C*H*$_3$)$_3$). ^{11}B (128 MHz, CD_2Cl_2, δ ppm) 12.00 (bs); $^{13}C\{^1H\}$ (100MHz, CD_2Cl_2, δ ppm) 127.67 (s, Ar-C), 127.62 (s, Ar-C), 67.73 (d, $^4J_{CP}$ 2.2 Hz, CH_2), 39.63 (d, $^1J_{CP}$ 29.3 Hz, *C*$(CH_3)_3$), 30.97 (d, $^3J_{CP}$ 13.9 Hz, CH_2), 30.14 (s, C(*C*H$_3$)$_3$), 22.35 (d, $^2J_{CP}$ 5.9 Hz, CH_2), 19.16 (d, $^1J_{CP}$ 36.0 Hz, CH_2) [partial]; $^{31}P\{^1H\}$ (161 MHz, CD_2Cl_2, δ ppm) 48.80 (s); Elemental Analysis $C_{22}H_{39}PB_2OCl_4$: Calculated C, 51.35 %; H, 7.65 %; Measured C, 51.78 %; H, 8.04 %.

Synthesis of $C_6H_4(BCl_2)_2CO_2PtBu_3$ (4): In a 100 mL Schlenk flask, 1,2-bis(dicloroboryl)benzene (100 mg, 0.42 mmol) was dissolved in toluene (15 mL). *tert*-Butyl-phosphine (84 mg, 0.42 mmol, 1.0 eq), dissolved in 5 mL of toluene, was added and the reaction mixture was allowed to stir for 15 min at ambient temperature. The solution 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 white, microcrystalline solid formed. The solvent was removed via pipette and the remaining solid was washed with toluene (2 x3 mL), and dried *in vacuo*. Yield 157 mg, 77%. $C_{19}H_{31}B_2Cl_4O_2P$, M: 485.86 g/mol Elemental Analysis: calculated for $C_{19}H_{31}B_2Cl_4O_2P$+1/6(C_7H_8): C 48.33; H 6.50; Found: C 48.28; H 6.46. ^{1}H NMR (400 MHz, CD_2Cl_2, 300K): δ = 7.36 (dd, $^3J_{HH}$=2.9 Hz, 3.4 Hz, 2H), 7.18 (dd, $^3J_{HH}$=2.9 Hz, 3.4 Hz, 2H), 1.58 (d, $^3J_{PH}$=14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 300K): δ = 156.3 (d, $^1J_{PC}$=94.6 Hz, *C*O_2), 129.6 (CH), 127.9 (CH), 41.7 (d, $^1J_{PC}$=19.8 Hz, P*C*(CH_3)$_3$), 30.7 (CH_3) ppm. Quarternary carbons of $C_6H_4B_2$ ring were not observed. ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 300K): δ = 48.4 (s) ppm, ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 300K): δ = 48.4 (s) ppm, ^{11}B NMR (128 MHz, CD_2Cl_2, 300K): δ = 18.0 ppm. IR: 1718.96 cm^{-1} (CO_2)

Synthesis of [B(C_6F_5)$_3$][$C_5H_6Me_4NH_2$]: As reported in V. Sumerin, F. Schulz, M. Nieger, M. Leskel, T. Repo, B. Rieger, *Angew. Chem. Int. Ed.* **2008**, *47*, 6001–6003.

Synthesis of [NorbonylHB(C_6F_5)$_2$][$C_5H_6Me_4NH_2$] (5): In a thick walled Young reaction flask equipped with a Teflon cap, bis-(pentafluorophenyl)borane (100 mg, 0.29 mmol) was suspended in pentane (2 mL). Norbornylene (27mg, 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 (41mg, 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%. $C_{28}H_{32}BF_{10}N$, M: 583,36 g/mol, Elemental Analysis, calculated for $C_{28}H_{32}BF_{10}N$: 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_2Cl_2, 300K): δ = 5.52 (br, 2H, N*H*$_2$), 1.55 (s, 12H, C*H*$_3$), 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_2Cl_2, 300K): δ = 58.4 (N*C*(CH_3)$_2$), 40.1 (B*C*H), 37.7, 37.2, 35.8 (NC(CH_3)$_2$*C*H_2), 34.8, 34.7, 34.1, 29.0, 27.8 (*C*H_3), 16.0 (NC(CH_3)$_2$$CH_2$*C*$H_2$) ppm, Carbons of C_5F_6 ring were not observed. ^{19}F NMR (376MHz, CD_2Cl_2, 300K): δ = -132.2 (d, $^3J_{FF}$=20.6 Hz, 4F, *o*-C_6F_5), -164.5 (dd, $^3J_{FF}$=20.6 Hz, 19.5 Hz 2F, *p*-C_6F_5), -166.5 (m, 4F, *m*-C_6F_5) ppm, ^{11}B NMR (128 MHz, CD_2Cl_2, 300K): δ=-17.2 (d, $^1J_{BH}$=81.0 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(dicloroboryl)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_2Cl_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_2NHBH_3, [B(C_6F_5)$_3$][HTMP], or [NorbonylHB(C_6F_5)$_2$][HTMP]), the mixture was allowed to react for various reaction times at room temperature. D_2O (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_2Cl_2, 300K): δ = 3.22 (d, $^1J_{CH}$=142Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 300K): δ = 48.8 (q, $^1J_{CH}$=142Hz) ppm.

The yield was determined by ‘H NMR spectroscopy using the 1,4-dioxane as internal standard.

Reaction times and yields:

Reducing agent	Reaction time at rt	Yield (based on P*t*Bu_3)
Me_2NHBH_3	15 min	34%
$[B(C_6F_5)_3][HTMP]$	24 h	15%
$[NorbonylHB(C_6F_5)_2][HTMP]$	60 min	57%