

Supplementary Information for

Selective Reduction of CO₂ to a Methanol Equivalent by B(C₆F₅)₃-activated Alkaline Earth Catalysis

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General Experimental Procedures

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox. NMR spectra were collected at 298 K on a Bruker AV300 spectrometer operating at 75.5 MHz (¹³C), 96.3 MHz (¹¹B). The spectra were referenced relative to residual solvent resonances. Solvents (toluene, hexane) were dried by passage through a commercially available (Innovative Technologies) solvent purification system, under nitrogen and stored in ampoules over molecular sieves. C₆D₆, d₈-toluene and d₈-THF were purchased from Fluorochem Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. Di-n-butylmagnesium (1.0 M solution in n-heptane), pinacolborane (HBpin), carbon dioxide (CO₂) and ¹³CO₂ were purchased from Sigma-Aldrich Ltd. and tris(pentafluorophenyl)borane was purchased from Alfa Aesar. All were used without further purification. [LMg N(Me₂)BH₂N(Me₂)BH₃] and [LCa(THF)(N(Me₂)BH₃)] (L = HC{(Me)CN(2,6-*i*Pr₂C₆H)}₂) were synthesised by literature procedures.¹

Synthesis of [HC{(Me)CN(2,6-¹PrC₆H₃)}₂MgHB(C₆F₅)₃], **8**.

In a glovebox, to a stirring solution of [LMg N(Me₂)BH₂N(Me₂)BH₃] (0.4 mmol, 222 mg) in toluene (10 mL) was added tris(pentafluorophenyl)borane (0.4 mmol, 204 mg). The mixture was stirred overnight after which time solvent was removed under reduced pressure to yield pure **8** as a colourless solid (0.38 g, 98%). ¹H NMR (d₈-Tol): 7.10 – 6.86 (6H, s, Ar-*H*), 4.84 (1H, s, NC(CH₃)CH), 3.03 (4H, sept, *J*_{HH} = 6 Hz,

$\text{CH}(\text{CH}_3)_2$), 1.64 (1H, s, MgH), 1.54 (6H, s, $\text{NC}(\text{CH}_3)\text{CH}$), 1.09 (12H, d, $J_{\text{HH}} = 6$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.97 (12H, d, $J_{\text{HH}} = 6$ Hz, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{d}_8\text{-Tol}$, 125.76 MHz): 172.1 ($\text{NC}(\text{CH}_3)\text{CH}$), 143.3 ($o\text{-C}_6\text{F}_5$), 142.7 ($o\text{-C-Dipp}$), 141.6 ($p\text{-C}_6\text{F}_5$), 126.3 ($p\text{-C-Dipp}$), 124.2 ($m\text{-C}_6\text{F}_5$), 123.5 ($m\text{-C-Dipp}$), 96.4 ($\text{NC}(\text{CH}_3)\text{CH}$), 28.7 ($\text{NC}(\text{CH}_3)\text{CH}$), 24.4 ($\text{CH}(\text{CH}_3)_2$), 24.2 ($\text{CH}(\text{CH}_3)_2$), 24.1 ($\text{CH}(\text{CH}_3)_2$). ^{11}B NMR ($\text{d}_8\text{-Tol}$, 96.6 MHz) -18.9 (d, $^1J_{\text{HB}} = 67$ Hz, $\text{HB}(\text{C}_6\text{F}_5)_3$). Anal. Calcd. for $\text{C}_{47}\text{H}_{42}\text{BF}_{15}\text{MgN}_2$: C, 59.11; H, 4.43; N, 2.93%. Found: C, 58.91; H, 4.57; N, 2.87%

Synthesis of $[\text{HC}\{(\text{Me})\text{CN}(2,6\text{-}^1\text{PrC}_6\text{H}_3)\}_2\text{CaHB}(\text{C}_6\text{F}_5)_3(\text{THF})]$, **9**.

In a glovebox, to a stirring solution of $[\text{LCa}(\text{THF})(\text{N}(\text{Me}_2)\text{BH}_3)]$ (0.4 mmol, 235 mg) in toluene (10 mL) was added tris(pentafluorophenyl)borane (0.4 mmol, 204 mg). The mixture was stirred overnight after which time solvent was removed under reduced pressure to yield pure **9** as a colourless solid (0.41 g, 98%). ^1H NMR ($\text{d}_8\text{-tol}$, 298 K) $\delta = 1.02$ (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.09 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.54 (s, 6H, $\text{NC}(\text{CH}_3)$), ca. 2.4 (coincident m, ca. 1H, BH), 2.97 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 4.80 (s, 1H, C-H), 6.95 – 7.16 (m, 6H, arom-H). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{d}_8\text{-tol}$, 298 K) $\delta = 24.8$ ($\text{CH}(\text{CH}_3)$), 24.9 ($\text{CH}(\text{CH}_3)$), 25.0 ($\text{CH}(\text{CH}_3)$), 25.5 ($\text{CH}(\text{CH}_3)$), 28.9 ($\text{NC}(\text{CH}_3)$), 124.5 ($m\text{-C}_6\text{H}_3$), 124.7 ($p\text{-C}_6\text{H}_3$), 141.8 ($o\text{-C}_6\text{H}_3$), 143.1 ($\text{HB}(m\text{-C}_6\text{F}_5)_3$), 145.2 ($\text{HB}(p\text{-C}_6\text{F}_5)_3$), 146.5 ($i\text{-C}_6\text{H}_3$), 146.9 ($\text{HB}(o\text{-C}_6\text{F}_5)_3$). ^{11}B NMR ($\text{d}_8\text{-tol}$, 298 K) $\delta = -22.4$ (d, $J = 86$ Hz, $\text{HB}(\text{C}_6\text{F}_5)_3$). ^{19}F NMR ($\text{d}_8\text{-tol}$, 298 K) $\delta = -134.1$ (br. s, 4F, $o\text{-C}_6\text{F}_5$), -159.3 (br. s, 2F, $p\text{-C}_6\text{F}_5$), -162.8 (br. s, 4F, $m\text{-C}_6\text{F}_5$). Anal. Calc. for $\text{C}_{51}\text{H}_{50}\text{BCaF}_{15}\text{N}_2\text{O}$: C: 58.74; H: 4.83; N: 2.69 %. Found: C: 58.62, 58.67; H: 4.76, 4.75; N: 2.62, 2.59%.

Synthesis of $[(\text{C}_6\text{F}_5)_3\text{BOC}(\text{H})\text{OC}(\text{H})\{(\text{Me})\text{CN}(2,6\text{-}^1\text{PrC}_6\text{H}_3)\}_2\text{MgO}_2\text{CH}]_2$, **10**

In a Youngs tap NMR tube, a solution of compound **8** (0.03 mmol, 30 mg) in $\text{d}_8\text{-THF}$ (0.5 mL) was freeze thaw degassed and exposed to ~1 atm of CO_2 . The sample was resealed and left at room temperature for two hours before NMR data were recorded. On concentration, the solution deposited crystals of compound **10** suitable for single crystal X-ray diffraction analysis (0.02 g, 64%). ^1H NMR ($\text{d}_8\text{-THF}$): 8.31 (1H, s, $^1J_{\text{HH}} = 219.16$ Hz, $\text{OC}(\text{H})\text{O}$), 7.09 – 6.96 (6H, s, Ar-H), 4.70 (1H, s, $^3J_{\text{HH}} = 7$ Hz, $\text{NC}(\text{CH}_3)\text{CH}$), 3.18-3.06 (3H, three overlapping sept., $^3J_{\text{HH}} = 6$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.98 (1H, sept, $^3J_{\text{HH}} = 6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.88 (6H, s, $\text{NC}(\text{CH}_3)\text{CH}$), 1.13, 1.08, 1.07, 1.02 (four 6H d, $^3J_{\text{HH}} = 6$ Hz, $\text{CH}(\text{CH}_3)_2$), $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{d}_8\text{-THF}$, 125.76 MHz): 182.7 ($\text{MgOC}(\text{H})\text{OMg}$), 173.5 ($\text{BOC}(\text{CH})\text{O}$), 172.1 ($\text{NC}(\text{CH}_3)\text{CH}$), 143.3 ($o\text{-C}_6\text{F}_5$), 142.7

(*o*-C-Dipp), 141.6 (*p*-C₆F₅), 126.3 (*p*-C-Dipp), 124.2 (*m*-C₆F₅), 123.5 (*m*-C-Dipp), 96.4 (NC(CH₃)CH), 28.7 (NC(CH₃)CH), 24.4 (CH(CH₃)₂), 24.2 (CH(CH₃)₂), 24.1 (CH(CH₃)₂). ¹¹B NMR (d₈-Tol, 96.6 MHz) -2.32 (s, OB(C₆F₅)₃). Anal. Calcd. for C₄₉H₄₂BF₁₅MgN₂O₄: C, 56.43; H, 4.06; N, 2.69%. Found: C, 55.81; H, 4.01; N, 2.64%

Figure S1: ¹H NMR spectrum of reaction of compound **8** with ¹³CO₂ immediately after introduction of the carbon dioxide illustrating the rapid adduct formation with the β-diketiminato ligand (doublet signal at 4.71 ppm).

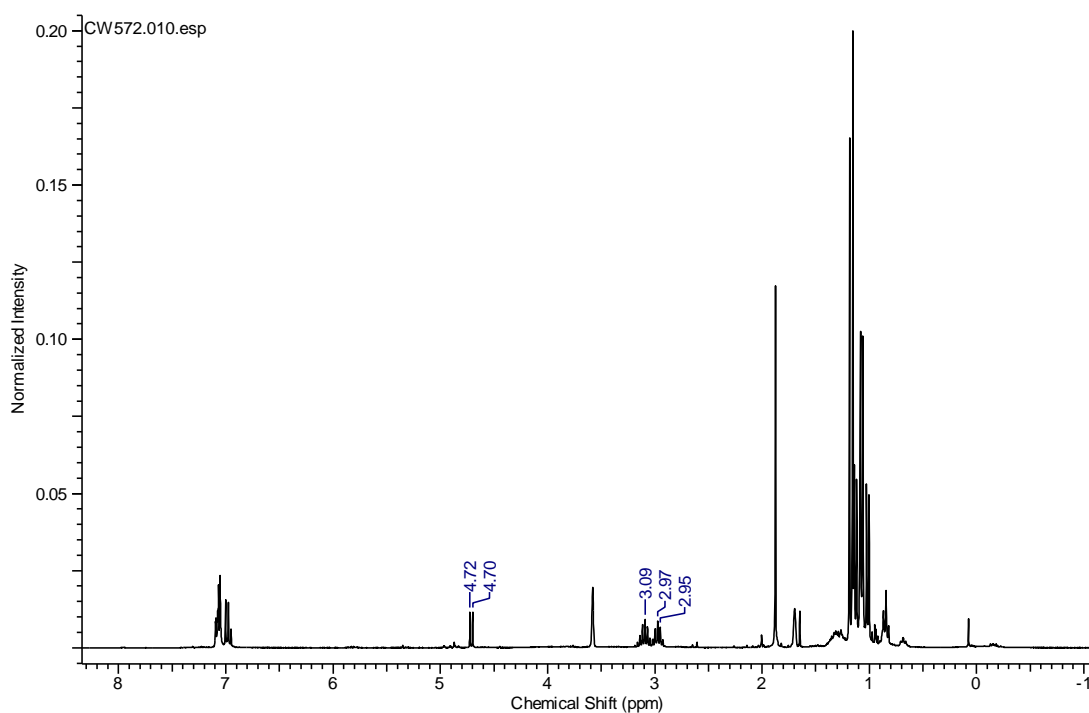


Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of reaction of compound **8** with $^{13}\text{CO}_2$ immediately after introduction of the carbon dioxide illustrating the rapid adduct formation with the β -diketiminato ligand (methine signal at 184.6 ppm).

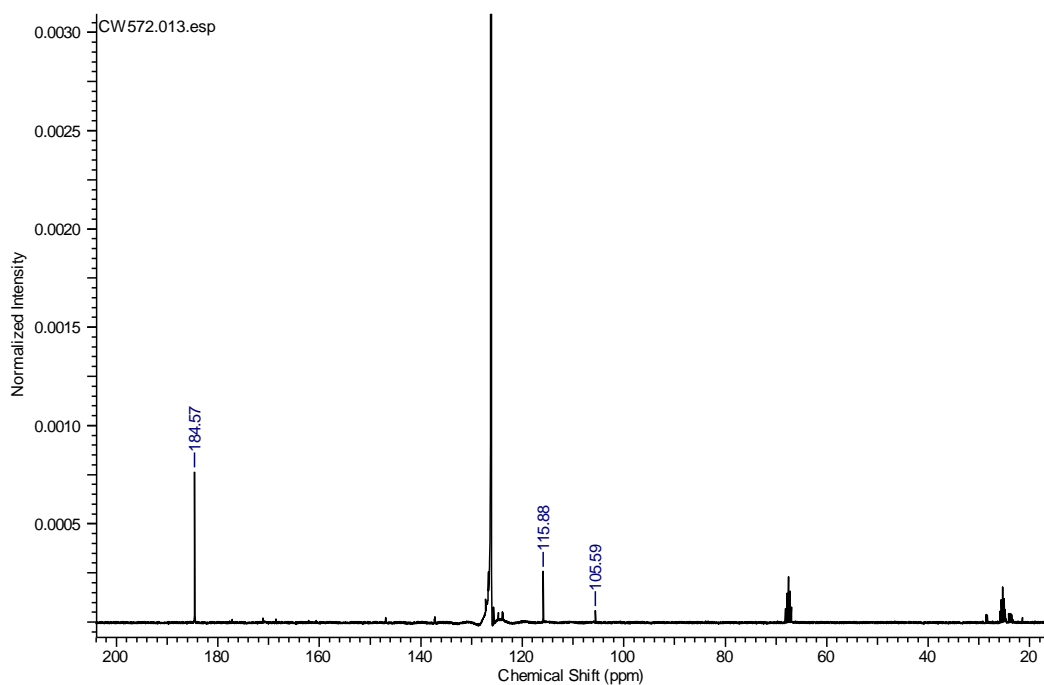


Figure S3: ^1H NMR spectrum of reaction of compound **8** with $^{13}\text{CO}_2$ after 15 hours illustrating the formation of the formate anion (doublet signal at 8.22 ppm).

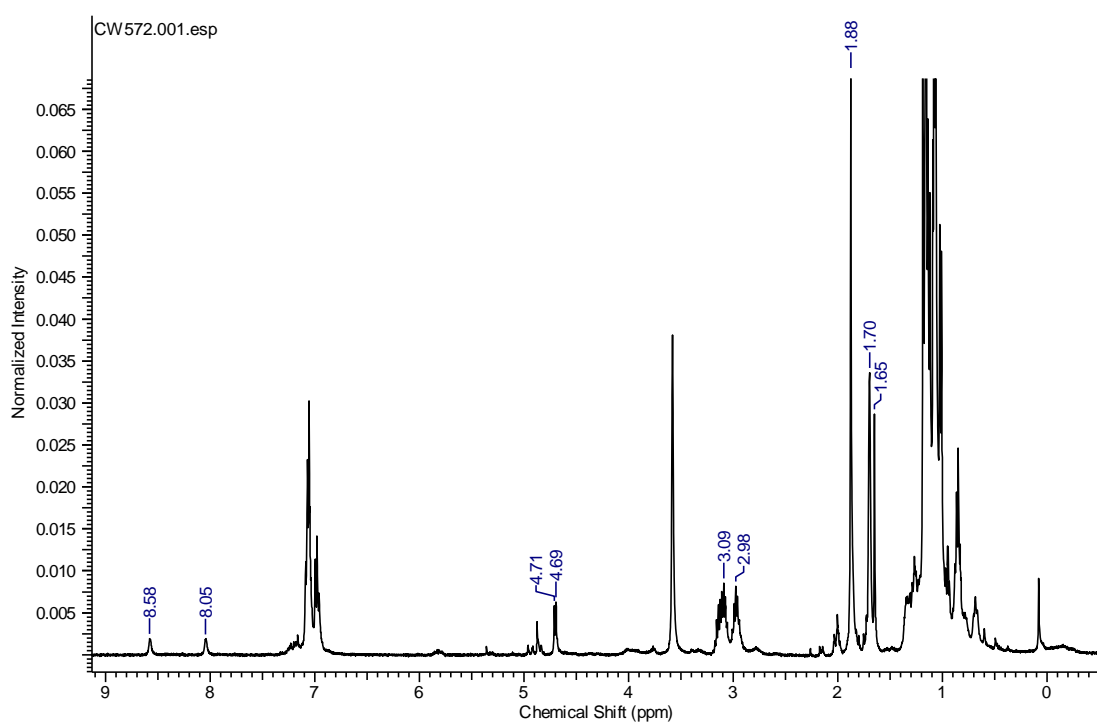


Figure S4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of reaction of compound **8** with $^{13}\text{CO}_2$ after 15 hours illustrating the formation of the formate anion (signal at 171.1 ppm).

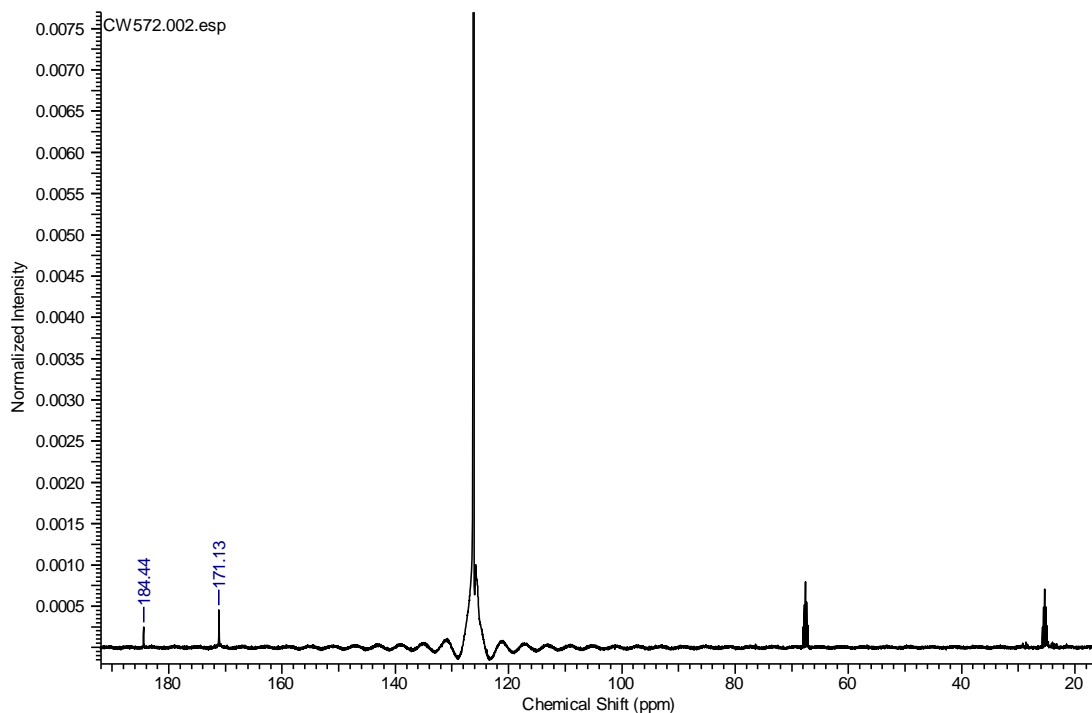
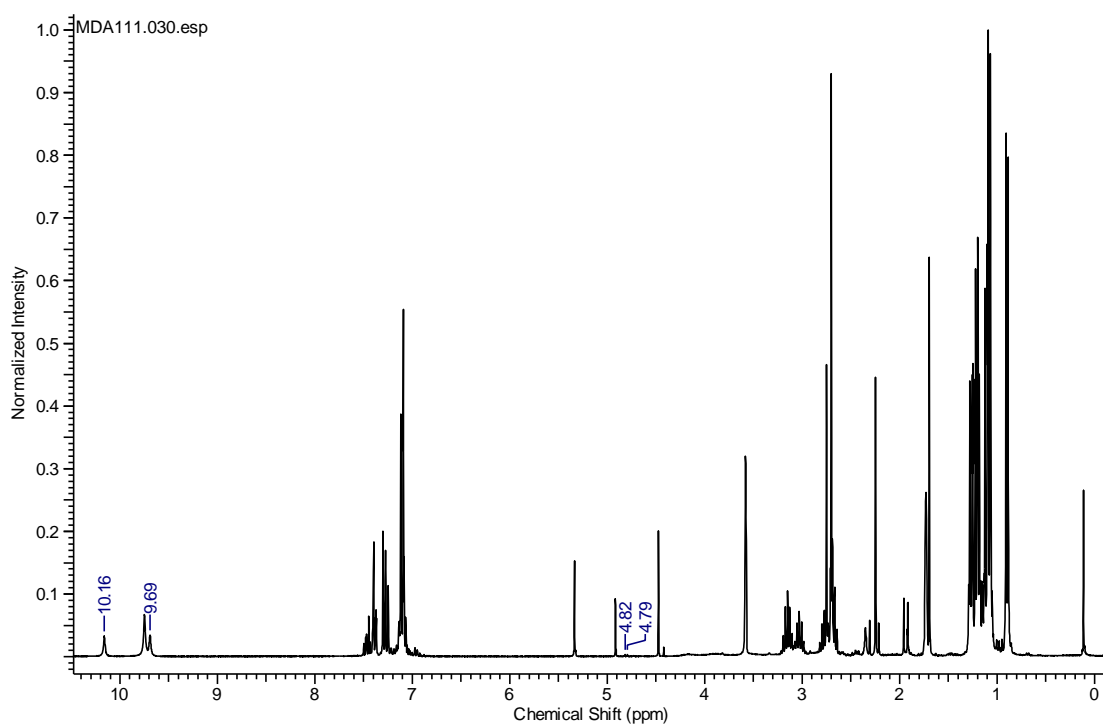


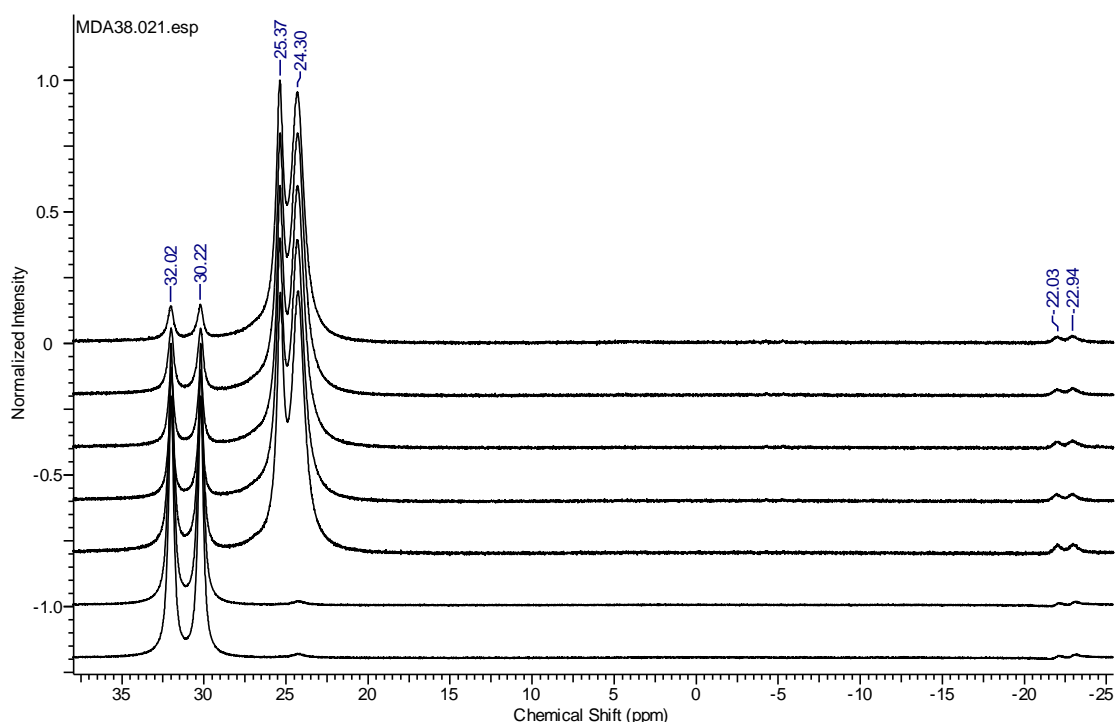
Figure S5: ^1H NMR spectrum of reaction of compound **8** with $^{13}\text{CO}_2$ after replacement of the $^{13}\text{CO}_2$ atmosphere with CO_2 illustrating the disappearance of the doublet signal at 4.70 ppm and retention of formate signal.



Catalytic hydroboration of CO₂

In a glovebox, to a vial containing compounds **8** or **9** or **10** (0.01 mmol), was added d₈-THF (0.5 mL) followed by HBpin (0.1 mmol). The resultant solution was transferred to a NMR tube equipped with a Youngs tap which was sealed and removed from the glovebox. The solution was then freeze pumped thawed to remove argon and exposed to ~1 atm of CO₂, resealed and warmed to 60°C. NMR analysis was performed at regular intervals and conversions were analyzed by ratios of starting material to product, with products identified by comparison to literature values.

Figure S6: ¹¹B NMR spectra recorded during catalysis by compound **8** after (bottom to top) 0, 10, 20, 30, 40, 50 and 60 hours illustrating the disappearance of the HBpin doublet signal (30.1 ppm) and the simultaneous formation of CH₃OBpin (25.3 ppm) and (pinB)₂O (24.3 ppm). The [HB(C₆F₅)₃][−] anion is observed to persist throughout the reaction at δ_{11B} 22.5 ppm.



Crystallographic experiments

Diffraction data for compounds **9** and **10** were collected on a Nonius Kappa CCD with a low temperature device at 150 K, utilizing Mo-K α radiation monochromated with graphite ($\lambda = 0.71070$ Å). Processing utilised the Nonius software,^{2,3} with structure solution and refinement using XSeed, SHELXS and SHELXL⁴ and visualized utilising ORTEP 3.⁵

Table S1. Crystal data and structure refinement for **9**

Identification code	k13msh29
Empirical formula	C ₅₁ H ₅₀ B Ca F ₁₅ N ₂ O
Formula weight	1042.82
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 12.5666(1) Å $\alpha = 90^\circ$ b = 19.7682(2) Å $\beta = 107.382(1)^\circ$ c = 20.4056(2) Å $\gamma = 90^\circ$
Volume	4837.65(8) Å ³
Z	4
Density (calculated)	1.432 Mg/m ³
Absorption coefficient	0.228 mm ⁻¹
F(000)	2152
Crystal size	0.60 x 0.50 x 0.40 mm
Theta range for data collection	3.53 to 27.48 °
Index ranges	-16 ≤ h ≤ 16; -25 ≤ k ≤ 25; -26 ≤ l ≤ 26
Reflections collected	66696
Independent reflections	11065 [R(int) = 0.0486]
Reflections observed (>2sigma)	8333
Data Completeness	0.996
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.913 and 0.824
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11065 / 19 / 672
Goodness-of-fit on F ²	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0388 wR2 = 0.0873
R indices (all data)	R1 = 0.0615 wR2 = 0.0974
Largest diff. peak and hole	0.254 and -0.239 eÅ ⁻³

Notes: Carbons C32 and C33 in the THF ligand are disordered over two sites in an 80:20 ratio. The minor fractional-occupancy carbons have been anisotropically refined subject to C-C distance and ADP restraints, in order to assist convergence. H1 (attached to B1) was located and refined freely.

Table S2. Crystal data and structure refinement for **10**

Identification code	h13msh5
Empirical formula	C _{56.80} H _{50.60} B F ₁₅ Mg N ₂ O ₄
Formula weight	1145.31
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 25.2580(8) Å alpha = 90° b = 12.8730(4) Å beta = 99.746(1)° c = 34.507(1) Å gamma = 90°
Volume	11057.9(6) Å ³
Z	8
Density (calculated)	1.376 Mg/m ³
Absorption coefficient	0.130 mm ⁻¹
F(000)	4715
Crystal size	0.30 x 0.25 x 0.07 mm
Theta range for data collection	3.57 to 25.03 °
Index ranges	-29<=h<=29; -15<=k<=15; -41<=l<=41
Reflections collected	43618
Independent reflections	9215 [R(int) = 0.0672]
Reflections observed (>2sigma)	5346
Data Completeness	0.944
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.997 and 0.889
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9215 / 7 / 741
Goodness-of-fit on F ²	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0761 wR2 = 0.1862
R indices (all data)	R1 = 0.1395 wR2 = 0.2228
Largest diff. peak and hole	0.405 and -0.340 eÅ ⁻³

Notes: The asymmetric unit comprises ½ of a dimer molecule (proximate to a crystallographic inversion centre), one full molecule of benzene and an additional ½ molecule of benzene at 60% occupancy. C56 and C59 from the latter are coincident with a 2-fold rotation axis intrinsic to the space-group symmetry. As such, these 2 fractional occupancy carbons atoms exhibit 30% occupancy. Distance restraints were applied to this solvent moiety to assist convergence. The crystal was a weakly diffracting at higher Bragg angles (plate); hence data were truncated to 25°.

References

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