Non-metal Mediated Homogeneous Hydrogenation of CO₂ to CH₃OH

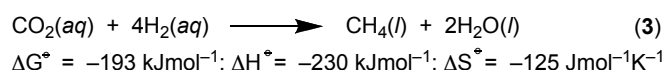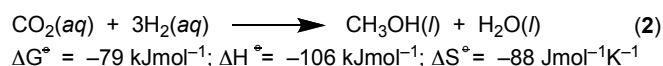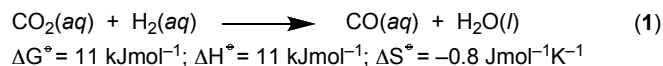*Andrew E. Ashley,* Amber L. Thompson and Dermot O'Hare**

The role of carbon dioxide as a greenhouse gas and its contribution to global warming is widely recognised by both scientists and governmental agencies.[1] It is now imperative that new reactions and processes are discovered that can either efficiently store or utilise the abundant and renewable CO_2 resource in an environmentally friendly manner. However, we face a fundamental challenge because carbon dioxide is so kinetically and thermodynamically stable.

The storage of the non polar CO_2 molecule in a solid proves difficult yet progress is being made using a range of high surface area macro and microporous materials such as inorganic materials (eg. alumina, silicas and zeolites), organic materials (eg. activated carbons), as well as complex metal-organic frameworks (MOFs).[2] Arguably a more desirable outcome would be the low temperature conversion of CO_2 into useful chemicals for both energy and as chemical feedstocks. Simultaneously this would have the additional benefit of reducing our requirements on fossil fuel reserves. Homogenous and heterogeneous processes have been developed that utilise CO_2 to produce CO, formic acid and its derivatives.[3] However, these reactions are far from ideal and so further breakthrough technologies are required.

Of particular interest is the reduction of CO_2 by H_2 to give renewable sources such as methanol (CH_3OH). CH_3OH is considered to be a valuable product because it can be safely stored and transported. World demand for CH_3OH is currently increasing enormously because of its role as a precursor to many useful organic chemicals (e.g., formaldehyde, acetic acid), as a substitute for fuels and for the generation of electricity in fuel cells. The hydrogenation of CO_2 to CH_3OH is thermodynamically favourable, but it is not the most favourable transformation of CO_2 with H_2 (Scheme 1). CO_2 hydrogenation has been extensively developed using solid oxide catalysts, but was only first reported in homogeneous solution by Sasaki and co-workers using $Ru_3(CO)_{12}$-KI mixtures.[4] However, these systems tend to give distributions of C_1 products, CO, CH_3OH and CH_4. Furthermore, we are not aware of the homogeneous conversion of CO_2 to CH_3OH using non-metal complexes.

In recent years Stephan has been developing the concept of "frustrated Lewis pairs" (FLPs).[5] These are systems in which the

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sterics imposed by the substituents on the donor and acceptor atoms prevents formation of a strong donor-acceptor interaction. In such situations the groups of Stephan, Erker, Repo/Rieger and others have shown that these Lewis acid/base combinations can heterolytically activate H_2.[6] These systems can then be subsequently used in metal-free catalytic hydrogenation and addition to olefins and other organic substrates.[7] Recently, Stephan has also shown that $B(C_6F_5)_3$ and tBu_3P in C_6H_5Br can reversibly bind carbon dioxide under mild conditions.[8]

$$CO_2(aq) + H_2(aq) \longrightarrow CO(aq) + H_2O(l) \quad \textbf{(1)}$$
$$\Delta G^\circ = 11 \text{ kJmol}^{-1}; \Delta H^\circ = 11 \text{ kJmol}^{-1}; \Delta S^\circ = -0.8 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$CO_2(aq) + 3H_2(aq) \longrightarrow CH_3OH(l) + H_2O(l) \quad \textbf{(2)}$$
$$\Delta G^\circ = -79 \text{ kJmol}^{-1}; \Delta H^\circ = -106 \text{ kJmol}^{-1}; \Delta S^\circ = -88 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$CO_2(aq) + 4H_2(aq) \longrightarrow CH_4(l) + 2H_2O(l) \quad \textbf{(3)}$$
$$\Delta G^\circ = -193 \text{ kJmol}^{-1}; \Delta H^\circ = -230 \text{ kJmol}^{-1}; \Delta S^\circ = -125 \text{ Jmol}^{-1}\text{K}^{-1}$$

Scheme 1. Thermodynamic parameters for the hydrogenation of CO_2 to various C_1 products.

Herein we report that we have exploited the heterolytic activation of hydrogen and subsequent insertion of CO_2 into the B–H bond to demonstrate for the first time a homogeneous process for the conversion of CO_2 to methanol.

The reaction of H_2 with an equimolar ratio of 2,2,6,6-tetramethylpiperidine (TMP) and $B(C_6F_5)_3$ has been documented by Sumerin *et al.*, to give the salt $[TMPH][HB(C_6F_5)_3]$ (**1**) (Scheme 2) in which the hydrogen molecule has undergone heterolytic fission.[9] We have found that admission of CO_2 to a toluene solution of **1** at 100°C produces the unique formato-borate complex $[TMPH][HCO_2B(C_6F_5)_3]$ (**2**) in quantitative yield; the reaction can be conveniently monitored using solution ^{19}F NMR.[10] The ^1H NMR (C_7D_8) spectrum of **2** reveals a *ca.* 2 ppm downfield shift of the NH_2 protons relative to **1** and also displays a septet resonance at 8.24 ppm (J_{HF} = 2 Hz), consistent with a H…F interaction between the formate proton and each of the six *ortho*-F's of the $B(C_6F_5)_3$ unit; this assignment was confirmed through selective heteronuclear ^{19}F decoupling experiments.[11] **2** displays a carbonyl stretch at 1662 cm^{-1} in its IR spectrum (CHCl₃).
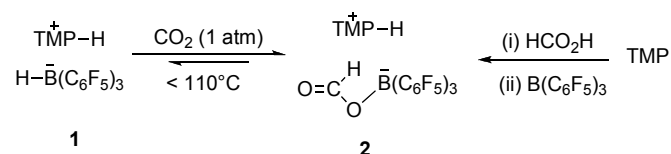
Scheme 2. Reversible reduction of CO_2 to formate (**2**) using H_2 activated by a frustrated Lewis acid-base pair (**1**). TMP denotes 2,2,6,6-tetramethylpiperidine (C_5Me_4NH).

Single crystals suitable for X-ray diffraction were grown by slow-cooling of a toluene solution of **2** to –35°C, (Figure 1).[12] While **2** exists as discrete ion-pairs, its B–O and C–O bond lengths more closely resemble the zwitterionic CO_2 adducts of the phosphine-based FLPs $tBu_3P(CO_2)B(C_6F_5)_3$ and *cyclo*-$(Me_3C_6H_2)_2PCH_2CH_2B(C_6F_5)_2(CO_2)$ (B–O: 1.5474(15)/1.550(4); C=O: 1.2081(15)/1.209(4); C–O: 1.2988(15)/1.284(4) Å, respectively),[8] rather than those found in $[Me_4N][(MeCO_2)B(C_6F_5)_3]$ (B–O: 1.514(2); C=O: 1.217(2); C–O:

1.324(2) Å).[13] The lengthening of the C=O bond observed for **2** is likely due to the participation of this group in H-bonding with two [TMPH] counterions, shown in Figure 1(b). Interestingly, no close H-*ortho*-F contacts are observed in the solid-state and it is possible that the optimisation of N-H....O$_2$CH hydrogen bonds dominates the crystal packing forces.

2 may also be synthesised in high yield by the reaction of TMP and HCO$_2$H to give [TMPH][HCO$_2$], and then subsequent reaction with B(C$_6$F$_5$)$_3$ (Scheme 2). This convenient protocol permits the regiospecific isotopic labelling of the formate moiety using H^{13}CO$_2$H to form [(C$_5$Me$_4$NH$_2$)H^{13}CO$_2$B(C$_6$F$_5$)$_3$] (**2a**) or DCO$_2$D in conjunction with TMP-d_1 (N-D) to give [(C$_5$Me$_4$ND$_2$)D^{12}CO$_2$B(C$_6$F$_5$)$_3$], in an atom-economical manner.

Heating a solution of **2** (C$_7$D$_8$) above 80°C in a sealed NMR tube under a N$_2$ atmosphere revealed that the formate complex is in equilibrium with free CO$_2$ (for **2a**; ^{13}CO$_2$ δ = 124.9 ppm in ^{13}C NMR) and **1**; using ^{19}F NMR we observed 2% of **2** has dissociated to give **1**.[14]
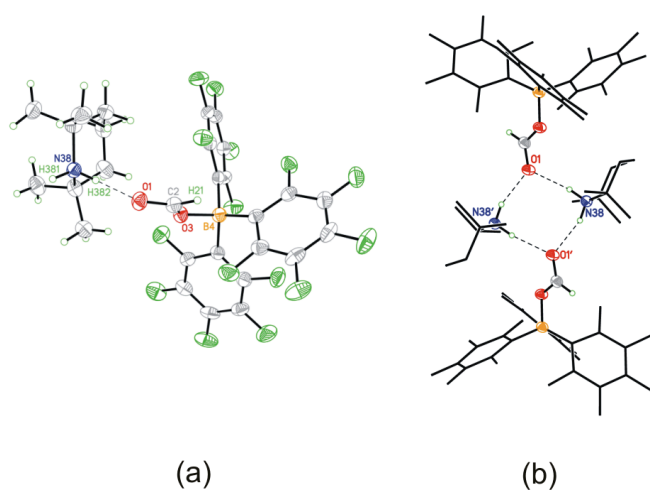

Figure 1. (a) Thermal ellipsoid plot of structure of one molecule in asymmetric unit of **2**. Hydrogen atoms on the TMP ring have been removed for clarity, thermal ellipsoids shown at 50 % probability. Selected bond lengths (Å): B4–O3 1.546(3); C2–O3 1.288(3); C2–O1 1.236(3); C2–H21 0.986; intramolecular distances for the second equivalent are statistically indistinguishable; (b) view showing the extended H-bonding motif; N38···O1 2.960(4)[2.857(4)] (H382···O1 2.04[1.99]); N38···O1' 2.853(4)[2.954(4)] (H381···O1 1.98[2.07]) analogous distances in the second equivalent shown in square brackets.

On heating **2a** above 110°C the reaction becomes partially irreversible by further reactions as judged by the ^{19}F NMR; after 24 hr at 160°C the production of C$_6$F$_5$H and two new major species are evident, one of these displaying broad resonances overlaying those observed for the *ortho*- and *para*-F of **2a**. The ^{1}H NMR spectrum is much simpler, showing a broadening and decreased intensity of the formate septet, a multiplet at 5.80 ppm (C$_6$F$_5$H), and the appearance of a doublet centred at 3.39 ppm (J$_{CH}$ = 146 Hz), characteristic of an sp^3-hybridised carbon environment.

Figure 2 shows the time dependence of the ^{13}C NMR of **2a** on heating at 160°C in toluene; the formate carbon resonance of **2a** (δ = 169.9 ppm, J$_{CH}$ = 210 Hz) is seen to collapse into a broad doublet after 24 hr (δ = 174.5 ppm, J$_{CH}$ = 230 Hz) which is concomitant with the appearance of a quartet (δ = 56.8 ppm, J$_{CH}$ = 146 Hz) and ^{13}CO$_2$, the latter two being the only species (above natural abundance ^{13}C) observable in the spectrum after 144 hr (Figure 2(c)); this clearly

demonstrates the almost quantitative conversion of the ^{13}C label present in **2a**. At this end-point of the reaction MS(FI) shows the homogeneous mixture to comprise of B(C$_6$F$_5$)$_3$, TMP, C$_6$F$_5$H and ^{13}CH$_3$OB(C$_6$F$_5$)$_2$ (^{11}B NMR δ = 35.9 ppm),[15] all of which are supported by ^{1}H, ^{19}F, ^{13}C and ^{11}B NMR spectral data. Furthermore, use of deuterium-labelled **2b** in this reaction gave C$_6$F$_5$D, CD$_3$OB(C$_6$F$_5$)$_2$ and N-deuterated TMP (^{2}H NMR δ(ppm) = 5.81, 3.30 and 1.16 respectively) as the only products incorporating deuterium. Overall this reaction represents a disproportionation of HCO$_2^-$ into CO$_2$ and CH$_3$O$^-$.
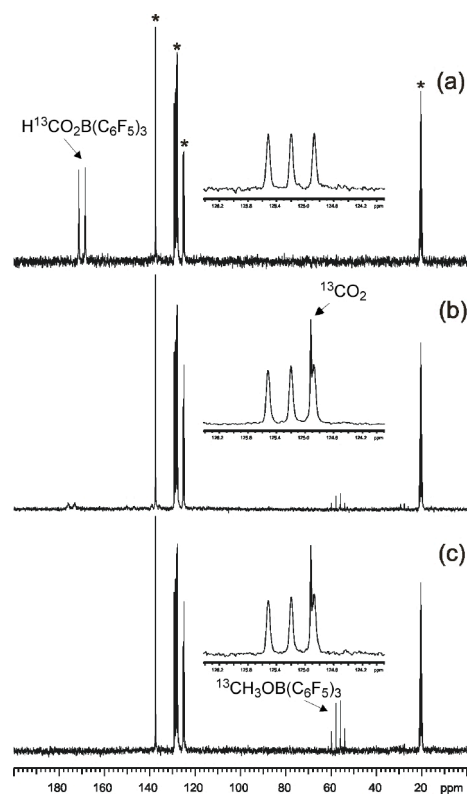

Figure 2. ^{13}C NMR spectra of **2a** after (a) 0 hr, (b) 24 hr and (c) 144 hr, at 160°C. * denotes peaks from solvent (C$_7$D$_8$); insets enhance region of ^{13}CO$_2$ resonance.

High-resolution mass spectrometry (ESI, –ve mode) of an aliquot of the reaction mixture after 24 hr heating at 160°C offered great insight into the mechanism. The MS exhibited ions which could be assigned to the borate anions in **1** and **2** in addition to the H$_2$O·B(C$_6$F$_5$)$_3$ H-bonded anions of HOB(C$_6$F$_5$)$_3$, CH$_3$OB(C$_6$F$_5$)$_3$, HCO$_2$B(C$_6$F$_5$)$_3$. Curiously, the species (C$_6$F$_5$)$_3$B(HCO$_2$)B(C$_6$F$_5$)$_3$ is also detected which could result from the reaction of HCO$_2$ B(C$_6$F$_5$)$_3$ with free B(C$_6$F$_5$)$_3$.

A proposed mechanism which takes into account all the experimental findings is shown in Scheme 3. The establishment of equilibrium concentrations of CO$_2$ and **1** from **2** is followed by reversible decomposition of the borohydride salt into free H$_2$, TMP and B(C$_6$F$_5$)$_3$; evidence for this process was established through ^{19}F NMR in which a solution of **1**, when heated to 160°C, shows the presence of 17% B(C$_6$F$_5$)$_3$. Attack of this B(C$_6$F$_5$)$_3$ upon the acyl oxygen atom of **2** produces an intermediate (Scheme 3, **A**) which is thought to be the origin of the broad doublet seen at 174.5 ppm in the ^{13}C NMR spectrum; the downfield shift and line-shape corroborate an augmented electron deficiency due to the coordination of an additional bulky B(C$_6$F$_5$)$_3$ molecule around a

2

single carbon centre. Following this, hydride reduction of the activated formate **A** by an equivalent of **1** leads to the formaldehyde acetal (intermediate **B**) and $B(C_6F_5)_3$. The instability of acetals in protic media towards an aldehyde and H_2O is well-documented,[16] and in this instance the [TMPH] counterions may serve as H^+ donors; cleavage of **B** to $H_2CO \cdot B(C_6F_5)_3$ (intermediate **C**) and **3** is by analogy. **C** is expected to be a potent electrophile and in the presence of **1** undergoes a final hydride reduction to form **4**. The absence of any reduction products between formate and methoxide indicates that the conversion of **A** to **B** is rate-determining, and is anticipated from the necessity of crowding three large $B(C_6F_5)_3$ molecules around a hindered formate in the reduction step.
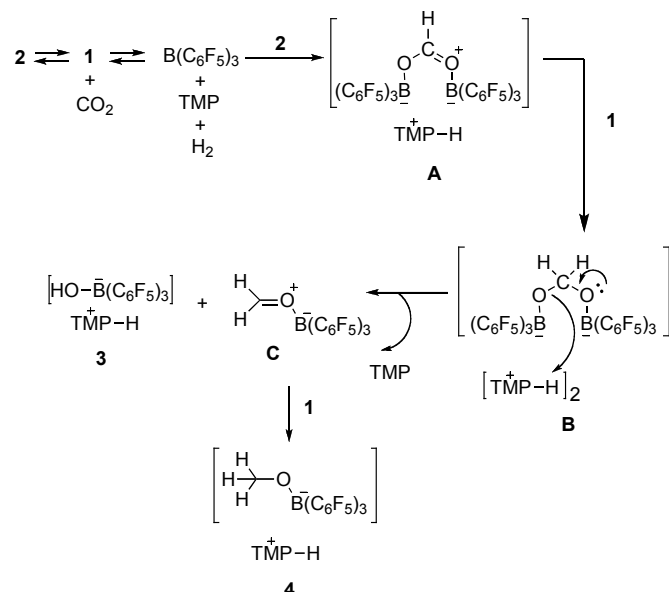
Scheme 3. Proposed mechanism for the disproportionation of **2** into **4** and CO_2.

To test the validity that **3** and **4** are formed in the reaction, these compounds were independently synthesised from either TMP and $H_2O \cdot B(C_6F_5)_3$[17] (1:1; **3**) or 1 eq. of anhydrous MeOH added to an equimolar mixture of TMP and $B(C_6F_5)_3$ (**4**). Heating a toluene solution (160°C) of the latter led to the rapid production of 1 eq. of C_6F_5H and $CH_3OB(C_6F_5)_2$, whilst that of the former was slower, proceeding to the boroxin $[OB(C_6F_5)]_3$[18] (presumably via $HOB(C_6F_5)_2$); all of these are identified as products in the completed reaction using ^1H, ^{19}F, ^{11}B NMR and MS (EI/FI).
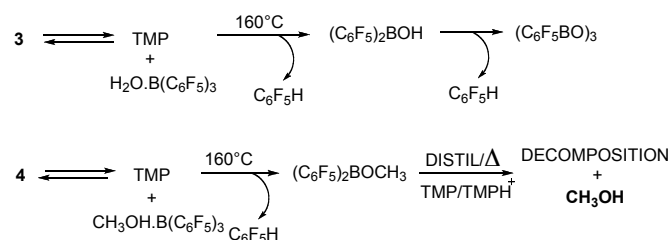
Scheme 4. Thermolysis of $[TMPH][HOB(C_6F_5)_3]$ (**3**) and $[TMPH][MeOB(C_6F_5)_3]$ (**4**), and production of CH_3OH.

Since the only labile source of protons in the decomposition reactions of **3** and **4** is the TMPH cation, this suggests that recombination of the ion pairs to form TMP and $ROH \cdot B(C_6F_5)_3$ (R = CH_3, H) must occur (Scheme 4); corroborating this hypothesis is the detection of $H_2O \cdot B(C_6F_5)_3$ H-bonded with various anions in the MS(ES).[19] Whilst studies have shown that such adducts can dissociate to give ROH and free $B(C_6F_5)_3$,[20] at these temperatures protonation of the *ipso*-C on the C_6F_5 rings appears to be faster (yielding $ROB(C_6F_5)_2$ and C_6F_5H), which preclude any catalytic turnover.

Finally, addition of one equivalent of CO_2 to a 1:1 mixture of $TMP/B(C_6F_5)_3$ (4 eq., excess, under H_2 atmosphere) in C_7D_8 demonstrated quantitative conversion to $CH_3OB(C_6F_5)_2$ via **2**, after 6 days at 160°C. Remarkably, vacuum distillation of the solvent (100°C) led to the isolation of CH_3OH (17-25% yield based on ^1H NMR integration against internal Cp_2Fe, and GC analysis) as the sole C_1 product, alongside C_6F_5H and TMP by-products. We expect that this results from the reaction of $CH_3OB(C_6F_5)_2$ with TMP or its conjugate acid.[21]

In conclusion we have demonstrated the first example of the selective hydrogenation of CO_2 to CH_3OH, using an FLP-based non-metal protocol at low pressures (1-2 atm). Current investigations are focussed on increasing the stability of the system towards hydroxylic agents, and hopefully thereby rendering the system catalytic.

Experimental Section

Experiments were conducted on a dual-manifold gas inlet/vacuum line or in a glove-box under a nitrogen atmosphere, unless indicated otherwise. Reaction solvents were dried using an MBraun SPS-800 solvent purification system and stored over K mirrors whilst NMR solvents were freeze-thaw degassed and stored over K (C_7D_8) or molecular sieves (CD_2Cl_2, DMSO-d_6). H_2 (BOC) and CO_2 (Sigma-Aldrich) were dried *via* passage through a column of molecular sieves prior to use. 2,2,6,6-tetramethylpiperidine (TMP, Sigma-Aldrich) was distilled and dried over 3 Å molecular sieves. HCO_2H (95% wt.%), DCO_2D (98% at.D) and $H^{13}CO_2H$ (Goss Scientific, 99% at.^{13}C). $B(C_6F_5)_3$ (sublimed prior to use),[22] $H_2O \cdot B(C_6F_5)_3$,[17c] TMP-d_1 (N-D)[23] and **1**[9] were synthesised according to literature procedures. The following instrumentation was used: Varian Mercury VX-Works 300 MHz for ^1H, ^2H, ^{13}C, ^{19}F (ext. $CFCl_3$ reference), ^{11}B (ext. $BF_3 \cdot OEt_2$ reference) NMR spectroscopy; an Enraf-Nonius FR590 KappaCCD diffractometer for X-ray diffraction; Waters GCT of EI/FI source or Bruker FT-ICR-MS Apex Qe (9.4 T, ESI in negative mode) for mass spectrometry. GC analysis was performed on a SGE BP1 (25 m, 0.53 I.D., 5 μm film) with 50°C hold (2.5 min) then 50°C min^{-1} ramp to 250°C method. Elemental microanalyses were conducted by Stephen Boyer at London Metropolitan University.

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[10] a) Even at room temperature (CO_2, 1 atm) this reaction proceeds to 18 % conversion in 12 hours; b) No indication of reaction of **1** with

CO is observable at temperatures up to 130°C; c) Interestingly, the system [*t*Bu$_3$PH][BH(C$_6$F$_5$)$_3$], [ref. 6(e)], does not react with CO_2 under the conditions successful for **1**.

[11] A similar effect has been demonstrated by a $^{19}F/^{1}H$ NOE experiment: J. M. Blackwell, W. E. Piers, M. Parvez, *Org. Lett.* **2000**, *2*, 695-698.

[12] The structure was solved by direct methods (SIR92) and refined by full-matrix least squares (CRYSTALS). CCDC-749113 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Crystal data for compound **2**: C$_{28}$H$_{21}$BF$_{15}$NO$_2$, M$_r$ = 699.26, crystal size (mm) = 0.06 x 0.10 x 0.10, triclinic, *P*-1, *a* = 11.6181(1), *b* = 14.9808(2), *c* = 17.5277(2) Å, α = 91.3525(5), β = 107.8912(6), γ = 100.6911(6)°, *V* = 2842.13(6) Å^3, *Z* = 4, ρ_{calcd} = 1.634 g cm^{-3}, μ = 0.169 mm^{-1}, Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), *T* = 150 K, $2\theta_{max}$ = 27.57°, 54455 measured reflections (12965 independent, R_{int} = 0.068), absorption correction (semi-empirical from equivalents), transmission factors 0.94/0.99, *R* = 0.0393, *wR* = 0.0904 refined against |*F*^{2}|, GOF = 0.9374, [$\Delta\rho$]$_{max}$ 0.44, [$\Delta\rho$]$_{min}$ -0.41 e Å^{-3}.

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CO₂ + H₂

MeOH
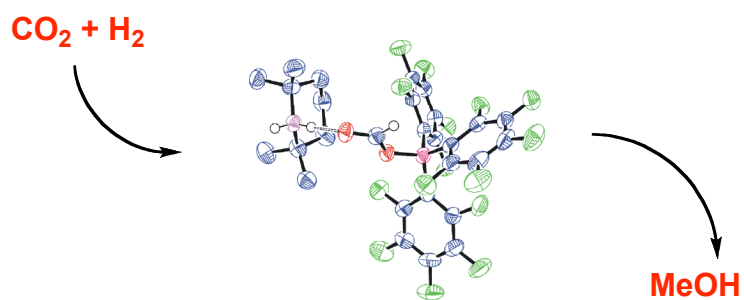
Addition of CO_2 to a toluene solution of 2,2,6,6-tetramethylpiperidine and $B(C_6F_5)_3$ under a H_2 atmosphere (1–2 atm) gives exclusively CH_3OH as the sole C_1-derived product, upon heating (160°C) and subsequent vacuum distillation. This is the first example of the selective homogeneous hydrogenation of CO_2 to CH_3OH utilising metal-free chemistry.