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Non-Metal-Mediated Homogeneous Hydrogenation of CO_2 to CH_3OH**

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The role of carbon dioxide as a greenhouse gas and its contribution to global warming are widely recognized by both scientists and governmental agencies.[1] It is now imperative that new reactions and processes are discovered for the efficient storage or utilization of the abundant and renewable CO_2 resource in an environmentally friendly manner. However, we face a fundamental challenge in that carbon dioxide is very kinetically and thermodynamically stable.

Storage of the nonpolar CO_2 molecule in a solid has proven difficult, yet progress is being made through the use of a range of high-surface-area macro- and microporous materials, such as inorganic materials (e.g. alumina, silicas, and zeolites), organic materials (e.g. activated carbon materials), and 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. The transformation of CO_2 in this manner would have the additional benefit of reducing our fossil-fuel requirements. Homogeneous and heterogeneous processes have been developed that utilize CO_2 to produce CO as well as 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 is considered to be a valuable product because it can be stored and transported safely. 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 in the generation of electricity in fuel cells. The hydrogenation of CO_2 to CH_3OH is thermodynamically favorable, but it is not the most favorable transformation of CO_2 with H_2 (Scheme 1). CO_2 hydrogenation has been developed extensively with solid oxide catalysts; it was first reported in homogeneous solution by Sasaki and co-workers, who used $[Ru_3(CO)_{12}]$/KI mixtures.[4] However, these systems tend to give mixtures of C_1 products: CO, CH_3OH, and CH_4. Furthermore, we are not aware of the homogeneous conversion of CO_2 into CH_3OH with nonmetal complexes.

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

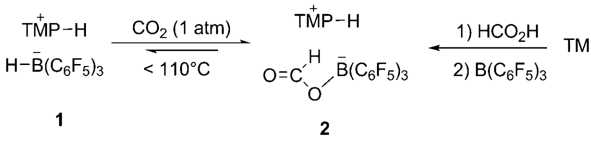
$$\mathrm{CO_2(aq) + 3H_2(aq) \longrightarrow CH_3OH(l) + H_2O(l)} \qquad (2)$$
$$\Delta G^{\ominus} = -79\ \mathrm{kJmol^{-1}};\ \Delta H^{\ominus} = -106\ \mathrm{kJmol^{-1}};\ \Delta S^{\ominus} = -88\ \mathrm{Jmol^{-1}K^{-1}}$$

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

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

In recent years, Stephan and co-workers have been developing the concept of "frustrated Lewis pairs" (FLPs).[5] In these systems, the steric environment imposed on the donor and acceptor atoms by the substituents prevents a strong donor–acceptor interaction. The research groups of Stephan, Erker, Repo and Rieger, and others have shown that such Lewis acid/base combinations can activate H_2 heterolytically.[6] These systems can be used in metal-free catalytic hydrogenation and addition to olefins and other organic substrates.[7] Recently, Stephan and co-workers also showed that $B(C_6F_5)_3$ and tBu$_3$P in C_6H_5Br can bind carbon dioxide reversibly under mild conditions.[8] Herein we describe the heterolytic activation of hydrogen and subsequent insertion of CO_2 into a B–H bond in the first homogeneous process for the conversion of CO_2 into methanol.

The reaction of H_2 with an equimolar mixture of 2,2,6,6-tetramethylpiperidine (TMP, Me_4C_5NH) and $B(C_6F_5)_3$ was documented by Sumerin et al. to give the salt [TMPH] $[HB(C_6F_5)_3]$ (**1**; Scheme 2), which results from heterolytic fission of the hydrogen molecule.[9] We found that the introduction of CO_2 into a solution of **1** in toluene at 100 °C produced the unique formatoborate complex [TMPH]-$[HCO_2B(C_6F_5)_3]$ (**2**) in quantitative yield; the reaction can be monitored conveniently by solution ^{19}F NMR spectroscopy.[10] The ^{1}H NMR (C_7D_8) spectrum of **2** revealed a downfield shift of the signals for the NH_2 hydrogen atoms of about



Scheme 2. Reversible reduction of CO_2 to formate **2** with H_2 activated by a frustrated Lewis acid–base pair **1**.

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2 ppm relative to the corresponding resonance for **1** and also displayed a septet resonance at 8.24 ppm ($J_{HF} = 2$ Hz), which is consistent with an H···F interaction between the formate hydrogen atoms and each of the six *ortho* F atoms of the $B(C_6F_5)_3$ unit; this assignment was confirmed through selective heteronuclear ^{19}F decoupling experiments.[11] A carbonyl stretch at 1662 cm^{-1} was observed in the IR spectrum ($CHCl_3$) of complex **2**.

Single crystals suitable for X-ray diffraction were grown by the slow cooling of a solution of **2** in toluene to −35 °C (Figure 1).[12] Although **2** exists as discrete ion pairs, its B−O and C−O bond lengths more closely resemble those of 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) Å, C=O: 1.2081(15)/1.209(4) Å, 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) Å, C=O: 1.217(2) Å, C−O: 1.324(2) Å).[13] The lengthening of the C=O bond observed for **2** is probably due to the participation of this group in H bonding with two $[TMPH]^+$ counterions (Figure 1 b). Interestingly, no close H–F_{ortho} contacts are observed in the solid state; it is possible that the optimization of N−H···O_2CH hydrogen bonds dominates the crystal packing forces.

Complex **2** may also be synthesized in high yield by the reaction of TMP and HCO_2H to give $[TMPH][HCO_2]$, and subsequent treatment with $B(C_6F_5)_3$ (Scheme 2). This convenient protocol enables the regiospecific isotopic labeling of the formate moiety with $H^{13}CO_2H$ to form $[(C_5Me_4NH_2)H^{13}CO_2B(C_6F_5)_3]$ (**2a**) or with DCO_2D in conjunction with [D$_1$]TMP (N-D) to give $[(C_5Me_4ND_2)D^{12}CO_2B(C_6F_5)_3]$ (**2b**) in an atom-economical manner.

The heating of a solution of **2** (C_7D_8) above 80 °C in a sealed NMR tube under an N_2 atmosphere revealed that the formate complex is in equilibrium with free CO_2 (for **2a**, $\delta(^{13}CO_2) = 124.9$ ppm in the ^{13}C NMR spectrum) and **1**; by ^{19}F NMR spectroscopy, we observed that 2% of **2** had dissociated to give **1**.[14]

When **2a** was heated above 110 °C, the reaction became partially irreversible as a result of further reactions, as judged by ^{19}F NMR spectroscopy. After 24 h at 160 °C, the production of C_6F_5H and two new major species was evident; one of these compounds displayed broad resonances which overlapped with those observed for the *ortho* and *para* F substituents of **2a**. The ^1H NMR spectrum was much simpler; it showed a broadening and decrease in the intensity of the formate septet, a multiplet at $\delta = 5.80$ ppm (C_6F_5H), and the appearance of a doublet centered at $\delta = 3.39$ ppm ($J_{C,H} = 146$ Hz), characteristic of an sp^3-hybridized carbon center.

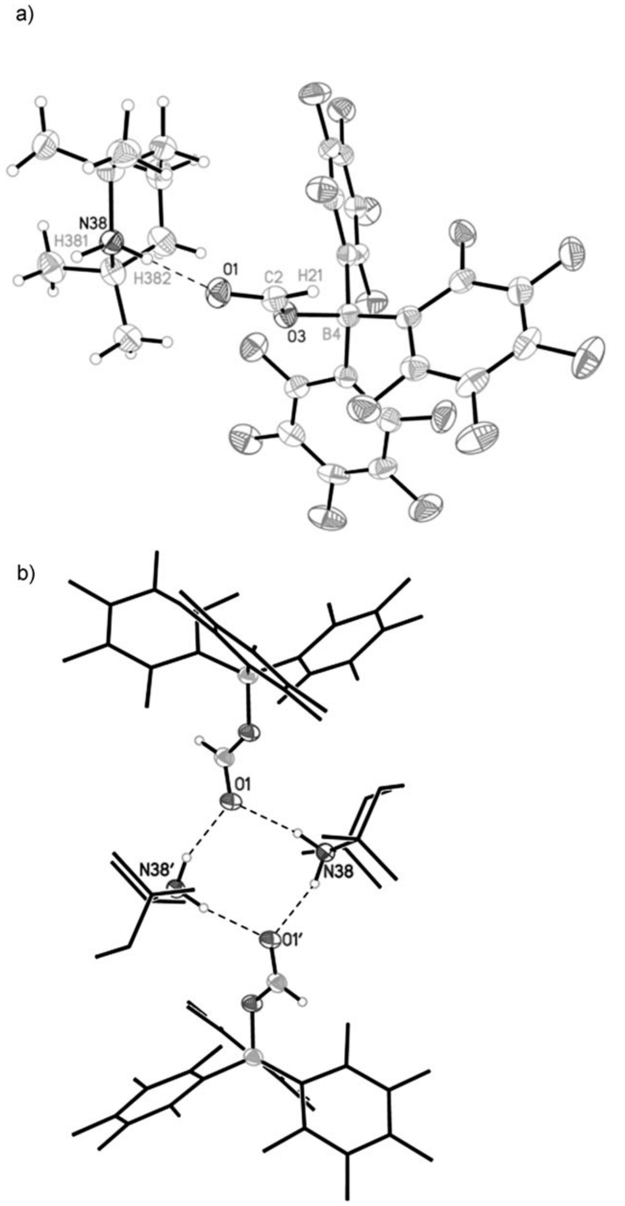


Figure 1. a) Thermal-ellipsoid plot of the structure of one molecule in the asymmetric unit of **2**. Hydrogen atoms on the TMP ring have been removed for clarity; thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å]: B4–O3 1.546(3), C2–O3 1.288(3), C2–O1 1.236(3), C2–H21 0.986;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

Figure 2 shows the time dependence of the ^{13}C NMR spectrum of **2a** on heating at 160 °C in toluene. The resonance for the formate carbon atom of **2a** ($\delta = 169.9$ ppm, $J_{C,H} = 210$ Hz) was observed to collapse into a broad doublet after 24 h ($\delta = 174.5$ ppm, $J_{C,H} = 230$ Hz); this change was concomitant with the appearance of a quartet ($\delta = 56.8$ ppm, $J_{C,H} = 146$ Hz) and the signal for $^{13}CO_2$. $^{13}CO_2$ and the compound responsible for the quartet were the only species (containing ^{13}C above natural abundance) observable in the spectrum after 144 h (Figure 2 c). This result clearly demonstrates the almost quantitative conversion of ^{13}C-labeled **2a**. At this end point of the reaction, field-ionization (FI) MS showed the homogeneous mixture to comprise $B(C_6F_5)_3$, TMP, C_6F_5H, and $^{13}CH_3OB(C_6F_5)_2$ (^{11}B NMR: $\delta = 35.9$ ppm),[15] the presence of all of which was supported by ^1H, ^{19}F, ^{13}C, and ^{11}B NMR spectral data. Furthermore, the use of deuterium-labeled **2b** in this reaction gave C_6F_5D, $CD_3OB(C_6F_5)_2$, and N-deuterated TMP (^2H NMR: $\delta = 5.81$, 3.30, and 1.16 ppm,

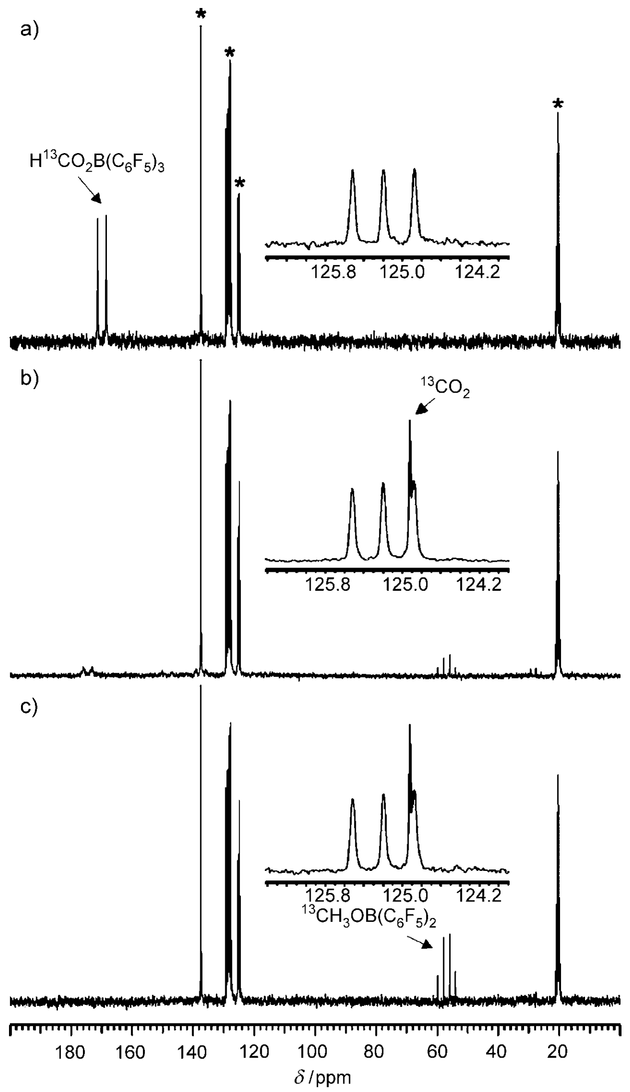
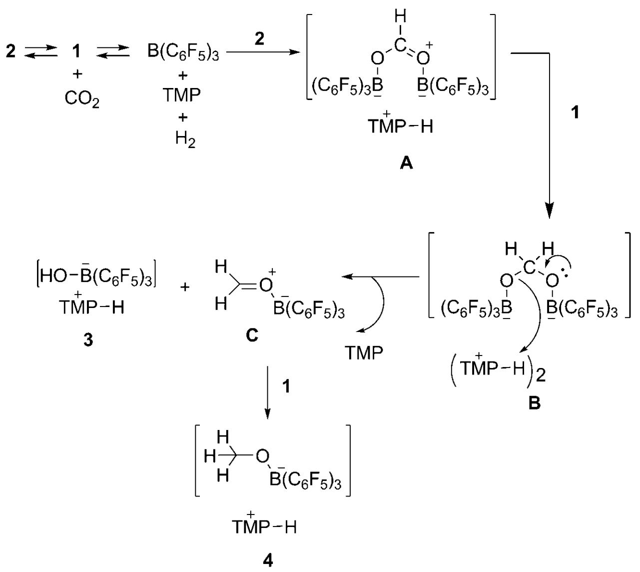


Figure 2. ^{13}C NMR spectra of **2a** after a) 0 h, b) 24 h, and c) 144 h at 160 °C. * denotes peaks from the solvent (C_7D_8); insets are magnifications of the region of $^{13}CO_2$ resonance.

respectively) as the only products that incorporated deuterium. Overall, this reaction represents a disproportionation of HCO_2^- into CO_2 and CH_3O^-.

High-resolution mass spectrometry (ESI, negative mode) of an aliquot of the reaction mixture after heating for 24 h at 160 °C offered great insight into the mechanism. Ions in the mass spectrum could be assigned to the borate anions in **1** and **2** as well as anions of $HOB(C_6F_5)_3$, $CH_3OB(C_6F_5)_3$, and $HCO_2B(C_6F_5)_3$ hydrogen-bonded to $H_2O{\cdot}B(C_6F_5)_3$. Curiously, the species $(C_6F_5)_3B(HCO_2)B(C_6F_5)_3$, which could result from the reaction of $HCO_2B(C_6F_5)_3$ with free $B(C_6F_5)_3$, was also detected.

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 $B(C_6F_5)_3$; evidence for this process was established through ^{19}F NMR spectroscopy, which showed the presence of 17 % $B(C_6F_5)_3$ after a solution of **1** was heated to 160 °C. The attack of $B(C_6F_5)_3$ on the acyl oxygen atom of **2** produces an intermediate **A** (Scheme 3), which is thought to give rise to the broad doublet observed at $\delta = 174.5$ ppm in the ^{13}C NMR spectrum; the downfield shift and line shape of this signal indicate increased electron deficiency due to the coordination of an additional bulky $B(C_6F_5)_3$ molecule near a single carbon center. Hydride reduction of the activated formate **A** by an equivalent of **1** then leads to the formaldehyde acetal (intermediate **B**) and $B(C_6F_5)_3$. The instability of acetals in protic media (their transformation into an aldehyde and H_2O) is well-documented.[16] In this instance, the $[TMPH]^+$ counterions may serve as H^+ donors in the cleavage of **B** to give $H_2CO{\cdot}B(C_6F_5)_3$ (**C**) and **3**. Intermediate **C** is expected to be a potent electrophile and undergoes a final hydride reduction in the presence of **1** 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.

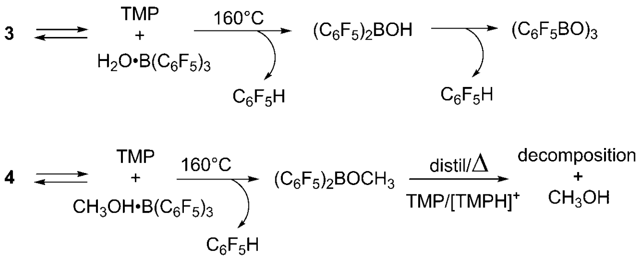


Scheme 3. Proposed mechanism for the disproportionation of **2** into **4** and CO_2.

To confirm that **3** and **4** were formed in the reaction, these compounds were synthesized independently from TMP and $H_2O{\cdot}B(C_6F_5)_3$[17] (1:1) in the case of **3**, and through the addition of anhydrous MeOH (1 equiv) to an equimolar mixture of TMP and $B(C_6F_5)_3$ in the case of **4**. Heating of a toluene solution of **4** prepared in this way at 160 °C led to the rapid production of 1 equivalent each of C_6F_5H and $CH_3OB(C_6F_5)_2$. The reaction of **3** under these conditions was slower and proceeded to the boroxin $(OB(C_6F_5))_3$[18] (presumably via $HOB(C_6F_5)_2$). All of these compounds (C_6F_5H, $CH_3OB(C_6F_5)_2$, and $(OB(C_6F_5))_3$) were identified by ^{1}H, ^{19}F, and ^{11}B NMR spectroscopy and MS (EI/FI) as products of the heating of **2** after completion of the reaction.

Since the only labile source of protons in the decomposition reactions of **3** and **4** is the TMPH cation, recombination of the ion pairs to form TMP and $ROH{\cdot}B(C_6F_5)_3$ (R =

CH_3, H) must occur (Scheme 4). This hypothesis was corroborated by the detection of $H_2O{\cdot}B(C_6F_5)_3$ hydrogen-bonded with various anions in the electrospray mass spectrum.[19]



Scheme 4. Thermolysis of $[TMPH][HOB(C_6F_5)_3]$ (**3**) and $[TMPH][MeOB(C_6F_5)_3]$ (**4**), and production of CH_3OH.

Although 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* carbon atoms on the C_6F_5 rings (to yield $ROB(C_6F_5)_2$ and C_6F_5H) appears to be faster, which precludes any catalytic turnover.

Finally, upon the addition of CO_2 (1 equiv) to a 1:1 mixture of $TMP/B(C_6F_5)_3$ (4 equiv) in C_7D_8 under an H_2 atmosphere, quantitative conversion into $CH_3OB(C_6F_5)_2$ via **2** was observed 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 integration of the ^1H NMR spectrum against internal Cp_2Fe and GC analysis) as the sole C_1 product, alongside C_6F_5H and TMP by-products. We expect that the formation of methanol results from the reaction of $CH_3OB(C_6F_5)_2$ with TMP or its conjugate acid (Scheme 4).[21]

In conclusion, we have demonstrated the selective hydrogenation of CO_2 to CH_3OH by using an FLP-based nonmetal-mediated procedure at low pressures (1–2 atm). Current investigations are focused on increasing the stability of the system towards hydroxylic agents with the hope of 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 by using an MBraun SPS-800 solvent-purification system and stored over potassium mirrors; NMR solvents were freeze–thaw degassed and stored over potassium (C_7D_8) or molecular sieves (CD_2Cl_2, [D_6]dimethyl sulfoxide). H_2 (BOC) and CO_2 (Sigma–Aldrich) were dried by 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 atom % D), and $H^{13}CO_2H$ (Goss Scientific, 99 atom % ^{13}C) were used. $B(C_6F_5)_3$ (sublimed prior to use),[22] $H_2O{\cdot}B(C_6F_5)_3$,[17c] [D_1]TMP (N–D),[23] and **1**[9] were synthesized according to literature procedures. The following instrumentation was used: a Varian Mercury VX-Works 300 MHz spectrometer for ^1H, ^2H, ^{13}C, ^{19}F (external $CFCl_3$ reference), and ^{11}B (external $BF_3{\cdot}OEt_2$ reference) NMR spectroscopy; an Enraf–Nonius FR590 KappaCCD diffractometer for X-ray diffraction; a Waters GCT (EI/FI source) or Bruker FT-ICR-MS Apex Qe spectrometer (9.4 T, ESI in negative mode) for mass spectrometry. GC analysis was performed on an SGE BP1 column (25 m, inside diameter: 0.53 mm, 5 μm film) with an initial temperature of 50 °C (hold, 2.5 min), then a 50 °C min^{-1} ramp to 250 °C. Elemental microanalyses were conducted by Stephen Boyer at London Metropolitan University.

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[10] Even at room temperature (CO_2, 1 atm), this reaction proceeded to 18% conversion in 12 h. No indication of the reaction of **1** with CO was observed at temperatures up to 130°C. Interestingly, the system [tBu$_3$PH][BH(C_6F_5)$_3$][6e] does not react with CO_2 under the conditions successful for **1**.

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[12] The crystal structure of **2** was solved by direct methods (SIR92) and refined by full-matrix least squares (CRYSTALS). Crystal data for **2**: $C_{28}H_{21}BF_{15}NO_2$, $M_r = 699.26$, crystal size: $0.06 \times 0.10 \times 0.10$ mm^3, triclinic, $P\bar{1}$, $a = 11.6181(1)$, $b = 14.9808(2)$, $c = 17.5277(2)$ Å, $\alpha = 91.3525(5)$, $\beta = 107.8912(6)$, $\gamma = 100.6911(6)$°, $V = 2842.13(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.634$ g cm^{-3}, $\mu = 0.169$ mm^{-1}, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 150$ K, $2\theta_{max} = 27.57°$, 54455 measured reflections (12965 independent, $R_{int} = 0.068$), absorption correction (semiempirical 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}. CCDC 749113 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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