A Highly Active Phosphine-Borane Organocatalyst for the Reduction of CO_2 to Methanol using Hydroboranes

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This is the peer reviewed version of the following article: [A Highly Active Phosphine-Borane Organocatalyst for the Reduction of CO2 to Methanol using Hydroboranes, J. Am. Chem. Soc. 2013, 135, 9326−9329], which has been published in final form at [10.1021/ja404585p].

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Supporting Information Placeholder

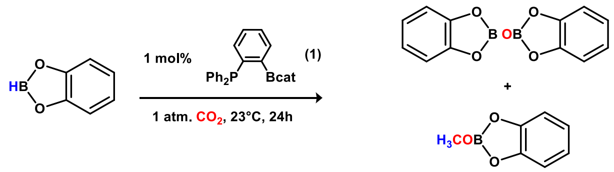
ABSTRACT: In this work, we report that organocatalyst 1-Bcat-2-PPh_2-C_6H_4 ((1); cat = catechol) acts as an ambiphilic metal free system for the reduction of carbon dioxide in presence of hydroboranes (HBR_2 = HBcat (catecholborane), HBpin (pinacolborane), 9-BBN (9-borabicyclo[3.3.1]nonane), and $BH_3.SMe_2$) to generate CH_3OBR_2 or $(CH_3OBO)_3$, products that can be readily hydrolysed to methanol. The yields can be as high as 99% with exclusive formation of CH_3OBR_2 or $(CH_3OBO)_3$ with TON (turn-over numbers) and TOF (turn-over frequencies) reaching >2,950 and 853 h^{-1}, respectively. Furthermore, the catalyst exhibits "living" behavior: once the first loading is consumed it resumes its activity on adding another loading of reagents.

It is widely known that carbon dioxide is a greenhouse gas and one of the most important contributors to global warming and several political initiatives have been put forward to reduce carbon dioxide emissions.[1] Most of the current systems known to catalyze the reduction of CO_2 into valuable products use transition metals,[2] including notably the reverse water-gas shift reaction to generate carbon monoxide which in turn can be transformed into several useful chemicals.[3] Recently, some homogeneous organometallic systems have shown promise in generating valuable chemicals[4]. The most active systems to date for the reduction of CO_2 into high hydrogen content molecules include a ruthenium phosphine complex[4c] and a nickel pincer complex[4d], using respectively H_2 and HBcat (HBcat = catecholborane), to generate MeOH from CO_2, and an iridium catalyst that can reduce CO_2 into methane using hydrosilanes as hydrogen source with turn-over numbers (TON) up to 8,300.[4e]

Recently, a variety of transition metal-free systems have emerged for carbon dioxide activation and functionalization. Indeed, it has recently been shown that Lewis acidic Et_2Al^+ species can catalytically reduce carbon dioxide to methane.[5] Similarly, silyl cations can catalytically reduce CO_2 to a mixture of benzoic acid, formic acid and methanol.[6] However, both systems greatly lack in selectivity and generate undesirable alkylation by-products. An avenue of interest for carbon dioxide activation is the use of "frustrated Lewis pairs" (FLP), work pioneered by Stephan and Erker.[7] Since this initial discovery, many ambiphilic systems have been shown to be active in the stoichiometric fixation CO_2.[8] Piers demonstrated elegant use of this concept for the catalytic reduction of CO_2 into methane using the robust TMP/$B(C_6F_5)_3$ (TMP = 2,2,6,6-tetramethylpiperidine) system with Et_3SiH, albeit with limited turnovers.[9] It has been shown that the FLP system consisting of $PMes_3/AlX_3$, (Mes = mesityl, X=Cl, Br) not only binds CO_2 but also reduces it to methanol using $BH_3.NH_3$ as hydrogen source.[10] Alternatively, O'Hare and Ashley demonstrated that CO_2 could be hydrogenated using TMP/$B(C_6F_5)_3$.[11] Unfortunately, the two last systems require stoichiometric amounts of FLP. Although interesting in concept, none of the FLP or ambiphilic systems reported to date demonstrate good catalytic activity for carbon dioxide reduction. The only efficient organocatalytic system reported to date for the reduction of CO_2 into methanol use highly Lewis basic N-heterocyclic carbene catalysts and diphenylsilane as hydrogen source with turn-over frequencies (TOF) of 25 h^{-1} at 25°C.[12]

Our research program targets ambiphilic systems with little "frustrated" character and/or weak Lewis acidity and basicity.[13] One ambiphilic system of interest is that of aryl bridged phosphine-boranes extensively studied by Bourissou and collaborators.[14] These molecules have been shown to be quite robust, stable and easy to synthesize. More recently, they have been used in the activation of singlet oxygen[15] and as organocatalysts for the Michael addition reaction[16], but to our knowledge the activity of these molecules for carbon dioxide reduction has not been investigated. Here we report that the 1-Bcat-2-PPh_2-C_6H_4 ambiphilic system is one of the most active catalysts for the selective catalytic reduction of carbon dioxide to methanol.

Although several ambiphilic phosphine-boranes were prepared by Bourissou[14-15], the synthesis of the catecholborane derivative 1-Bcat-2-PPh_2-C_6H_4 (**1**, Scheme 1) was never reported. The air-stable product is easily synthesized in 80% yield from previously reported o-lithiated triphenylphosphine using a known synthetic pathway (Figure S1, ESI).[17] Multinuclear NMR characterization of species **1** demonstrates this molecule to be monomeric in solution having no observable P-B interaction. The $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR chemical shifts are respectively of -4.57 and 33.1 ppm. The solid state structure (see ESI Figure S24) does not show any evidence of P-B interaction, the latter distance being quite long (3.28 Å).



Scheme 1. Reduction of CO_2 in presence of HBcat and catalyst 1.

Unsurprisingly, exposing **1** to 1 atmosphere of CO_2 at room temperature resulted in no spectroscopic change in solution (^1H, ^{31}P, and ^{11}B NMR spectroscopy). Although no adduct was observed between CO_2 and **1**, the addition of 100 equivalents of HBcat to a 9 mM solution of **1** in benzene-*d6* in a J-Young NMR tube under one atmosphere of CO_2 resulted in the formation of a white precipitate after 24 hours. This was characterized as catBOBcat based on spectroscopic comparison with the independently synthesized product (see Scheme 1). Monitoring of the solution using ^1H NMR spectroscopy showed the presence of a single new peak at 3.37 ppm attributed to CH_3OBcat by comparison to the independently synthesized product. Hydrolysis of the latter product produces methanol, which was confirmed using GC-FID. As expected, carrying out the same reaction under an atmosphere of $^{13}CO_2$ shows the formation of $^{13}CH_3OBcat$ with the expected $^1J_{C\text{-}H}$ of 145 Hz.[4d]

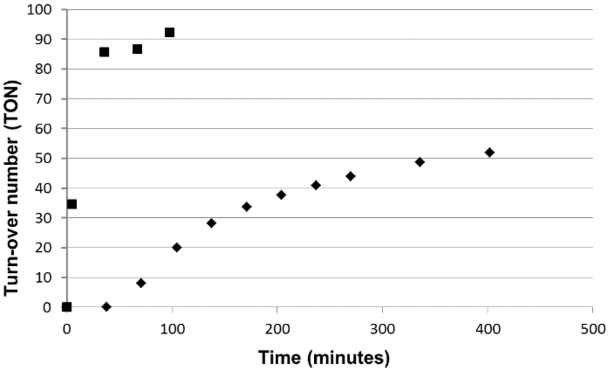


Figure 1. Turn-over numbers (TON) for the formation of CH_3OBcat from a 9 mM solution of **1** in benzene-*d6* in the presence of 100 equivalents of HBcat under one atmosphere of CO_2. The TON's are based on the number of hydrogen atoms transferred to CO_2. Reactions were carried out at (♦) 23°C and (■) 70 °C.

Monitoring the reduction of CO_2 in presence 100 equivalents of HBcat and **1** using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed an induction period of 30 minutes where no spectroscopic change was observed in the solution. However, after the induction period the reaction started readily and after 2 hours a 34% yield (TON = 34, TOF = 17 h^{-1}) of CH_3OBcat was obtained (Figure 1, ♦). The rate of the reaction diminished as the reaction progressed, suggesting that conversion is dependent on the concentration of HBcat in solution. Indeed, 50% conversion to CH_3OBcat was obtained in less than 5 hours and a yield of 69% of CH_3OBcat was observed after a period of 24 hours. The reduction of CO_2 also proceeded in the presence of 100 equivalents of $BH_3.SMe_2$ to generate $(CH_3OBO)_3$ but a longer induction period was observed (> 2 hours; Figure 2, ♦). Nevertheless, the conversion to the methoxyborane species is rapid once catalysis starts, obtaining respectively 108 and 200 TON at 2 and 5 hours after the induction period (respective TOF of 54 and 40 h^{-1}). After a period of 14 hours, a TON of 257 was obtained. The TON numbers being greater than 100 suggests that all hydrogen atoms from $BH_3.SMe_2$ are available for the reduction of CO_2. To our knowledge, it represents the first time that BH_3 is used as a hydrogen source for the catalytic reduction of CO_2 to methanol. It is interesting that the catalyst remains active even if BH_3 is known to coordinate phosphine moieties, which could inhibit catalysis; it is thus logical to presume that the longer induction period is caused by a competition between BH_3 and CO_2 for coordination to the catalyst. BH_3 is of great interest since it has the highest hydrogen content of any hydroborane.

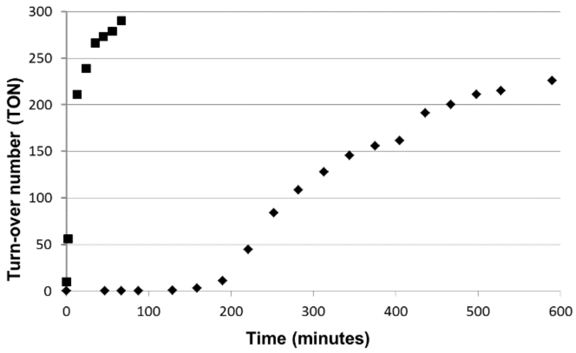


Figure 2. Turn-over numbers (TON) for the formation of $(CH_3OBO)_3$ from a 9 mM solution of **1** in benzene-*d6* in the presence of 100 equivalents of $BH_3.SMe_2$ under one atmosphere of CO_2. The TON's are based on the number of hydrogen atoms transferred to CO_2. Reactions were carried out at (♦) 23°C and (■) 70 °C.

A factor that dramatically increased the efficiency of the catalytic system was temperature. Heating a solution of **1** with 100 equivalent of HBcat to 70 °C under one atmosphere of CO_2 generated CH_3OBcat without any observable induction period (Figure 1, ■). After 36 minutes, a TON of 86 was observed (TOF = 143 h^{-1}), which increased to 92 after a period of 90 minutes (Table 1, entries 1-2). After letting the solution rest for a 24-hour period, another loading of 100 equivalents of HBcat was added and the solution reheated to 70 °C. The catalytic reaction resumed, but with a rate that seemed somewhat slower (an overall TON of 136 after 30 minutes), possibly due to the presence of a large quantity of precipitate in the solution (catBOBcat) that reduced the homogeneity of the solution. However, 60 minutes after the addition of the second loading a TON of 185 was measured (Table 1, entries 3-4), a similar yield to that observed in the first run. Such behaviour is reminiscent of a durable and "living" catalyst. Under similar conditions, $BH_3.SMe_2$ proved to be an excellent hydrogen source, generating 90% yield of $(CH_3OBO)_n$ in 67 minutes (TON = 271). A TON of 211 was obtained after only 13 minutes, representing a TOF of 973 h^{-1} (Figure 2, ■). The latter result is remarkable since the highest TOF reported for the reduction of CO_2 for a methanol derivate is 495 h^{-1} by a homogeneous nickel catalyst using HBcat as an hydrogen source.[4d] The reaction was also carried out using other hydroborane sources. The addition of 100 equivalent of HBpin to a solution of **1** under one atmosphere of CO_2 at 70°C generated 60% yield of the desired product in a 3 hour period (Table 1, entry 6). The significantly lower activity of the latter borane compared to HBcat is not surprising since it is known that HBpin is less reactive for the hydroboration reaction.[18] Similarly, 9-BBN only showed 34 TON in a 3-hour period (entry 7).

Table 1. Reduction of CO_2 with various hydroboranes[a]

Entry	Borane	#eq.	Time (min)	TON[b]	TOF (h^{-1})
1	HBcat	100	36	86	143
2	HBcat	100	98	92	56
3	HBcat	100+100[c]	30	136	72
4	HBcat	100+100[c]	60	185	85
5	$BH_3.SMe_2$	100	67	271	242
6	HBpin	100	174	60	21
7	9-BBN	50[d]	174	34	12
8[e]	HBcat	300	60	145[g]	145
9[f]	HBcat	1,000	240	664[g]	166
10[e]	$BH_3.SMe_2$	300	60	853[g]	853
11[f]	$BH_3.SMe_2$	1,000	240	>2,950[g]	>737
12[f]	$BH_3.THF$	300	60	340[g]	340

[a] Reaction conditions : Unless noted otherwise, 2.0 mg (0.0053 mmol) of **1** in 0.6 mL of benzene-d_6 at 70 °C [b] Based on mole of B-H consumed per mole of **1**, determined by ^{1}H NMR integration using hexamethylbenzene as internal standard for entries 1-7, and determined by GC-FID with iPrOH as standard for entries 8-11. [c] A second addition of 100 equivalents of HBcat was added 24 hours after the first addition. [d] Limited at 50 equivalents because of low solubility of 9-BBN. [e] 2.0 mg (0.0053 mmol) of **1** in 3 mL of benzene at 70 °C under *ca.* 2 atmosphere of CO_2. [f] 2.0 mg (0.0053 mmol) of **1** in 9 mL of benzene at 70 °C under *ca.* 2 atmosphere of CO_2. [g] Quenched with excess H_2O and analyzed by GC-FID with ^{i}PrOH as an standard.

Since diffusion problems could limit the rate of the reaction when carried out in NMR conditions, catalytic tests were carried out on a larger scale using Fisher-Porter bottles under *ca.* 2 atmospheres of CO_2. The products obtained were hydrolyzed to methanol and the turn-over numbers were calculated based on the concentration of methanol using gas chromatography with a flame ionisation detector. As can be observed in Table 1, the activities observed at the NMR scale can be reproduced at larger scale and lower catalyst loading. Indeed, the reduction of CO_2 using 300 equivalents of HBcat and $BH_3.SMe_2$ gave in one hour methanol in 48% and 95% yield, giving respectively TOF of 145 and 853 h^{-1} (Table 1, entries 8-9). It is notable that the TOF observed under large loading of hydroboranes are consistent to those observed at the NMR scale at low conversion that were respectively of 143 and 973 h^{-1} for HBcat and $BH_3.SMe_2$. Catalysis using a 0.1% catalyst loading (1000 equivalents of substrate) in a four hour period also gave impressive results. In the presence of HBcat, a TON of 664 was observed, which indicates that the rate of reaction remains the same during the four-hour period even with a lower catalyst loading and a lower catalyst concentration (Table 1, entry 10, TOF = 166 h^{-1}). In presence of $BH_3.SMe_2$, all of the substrate was consumed since the conversion to methanol was quantitative (Table 1, entry 11), once more suggesting that the TOF observed after one hour is conserved over a longer reaction time. The reaction works also with $BH_3.THF$, albeit less efficiently (Table 1, entry 11, TOF = 340 h^{-1}).

Density functional theory studies at the B3PW91 6-31G** level of theory were performed to obtain further insight at the mechanistic pathway, using HBcat as the hydrogen source. It should be noted that only potential intermediates were considered in the following and the results are summarized in Figure 3. Also, we did not account for the fact that HBCat is known to degrade in presence of Lewis bases since control experiments have shown this process to be marginal in our system.[19] As observed experimentally, the coordination of CO_2 to **1** to generate intermediate **IM1** is disfavoured by 9.9 kcal.mol^{-1}, in line with a weak coordination of carbon dioxide as reflected by its geometry. Indeed, despite the bending of the molecule (indicative of CO_2 activation), the C-O bonds appear to be only slightly elongated compared to free CO_2 (1.28 and 1.21 Å). Nevertheless, this adduct can undergo addition of HBcat to yield a novel species whose formation is favourable by 14.4 $kcal.mol^{-1}$ compared to **1**. Once the formation of the complex **IM2** is achieved, the second reduction to generate the formaldehyde-**1** adduct (**IM3**) and catBOBcat is downhill by 33.3 $kcal.mol^{-1}$. The third reduction to regenerate the catalyst as well as CH_3OBcat is an even more exothermic process (34.0 $kcal.mol^{-1}$). To summarize, as soon as the difficult coordination of CO_2 has taken place, the reduction is thermodynamically highly favourable.

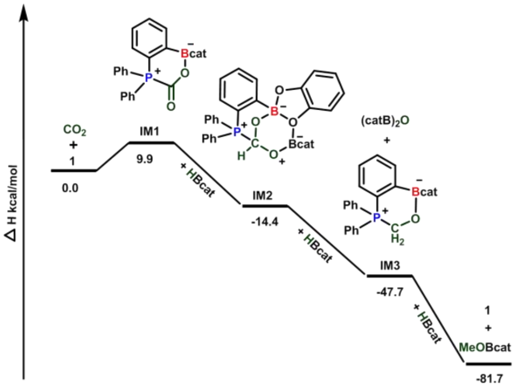


Figure 3. Enthalpy profile (in kcal/mol) for the reduction of CO_2 by **(1)** and catecholborane.

In order to confirm these computational results, **1** was reacted with methylformate in attempt to generate an analogous compound to **IM2**, namely species **IM2mf** (see Figure S22, Supporting Information). In line with the DFT results, where the adduct is predicted to be 3.9 $kcal.mol^{-1}$ higher in energy than **1**, no product could be observed by NMR spectroscopy. However, upon the addition of 3 equivalents of catecholborane *without the presence of* CO_2, a 90% conversion to CH_3OBCat was observed after 20 hours at room temperature. This latter results suggest that although the formation of the adduct **IM2mf** is thermodynamically slightly disfavoured, the reduction occurs in presence of a hydroborane. It is also interesting to note that the intermediate **IM3** is proposed to be formed in both reduction pathways. A similar formaldehyde intermediate was identified as a key intermediate in previous systems[4d,12], but could not be observed experimentally. While monitoring the reduction of CO_2 in presence of hydroboranes and catalyst **1**, only one resonance in the ^1H NMR spectra, a broad singlet at 5.20 ppm, could not be assigned to the starting materials or products. Running the experiment in presence of $^{13}CO_2$ allowed the observation of a $^1J_{C\text{-}H}$ of 151 Hz, suggesting that this species arise from the reduction of CO_2. In the later experiment, a $^1J_{P\text{-}C}$ of 52 Hz was also observed both in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. The latter species could not be isolated from the catalytic mixture, being in too small concentration in solution. However, when a solution of **1** was reacted with paraformaldehyde and heated at 70 °C for 15 minutes, the same product was observed to be formed with 74% conversion, as characterized by multinuclear NMR spectroscopy as **IM3** (see Supporting figure S19).

In summary, we have reported a metal free system for the reduction of carbon dioxide to methanol using a borane as reducing agent. The system is a robust living catalytic system and generates TOF up to 973 h^{-1} and TON up to 2950 at 70°C under 1 atm of CO_2, although larger TON can be expected by additional loadings of hydroboranes. The key aspect of this reported system compared to the other metal free systems for the activation of CO_2 is the weak interaction between the catalyst and carbon dioxide. Indeed, contrary to most ambiphilic and FLP systems reported to date, no adduct formation is observed between **1** and CO_2. Nevertheless, CO_2 being an ambiphilic molecule with its electrophilic carbon atom and nucleophilic oxygen atoms available, does not require significant bonding interaction with an ambiphilic catalyst to undergo reduction with hydroboranes. Once the first reduction has occurred, following reductions occur readily to generate CH_3OBR_2. Preliminary results demonstrate that the BPin analogue 1-Bpin-2-PPh_2-C_6H_4[15] is an active catalyst for the CO_2 reduction using $BH_3.SMe_2$, albeit working less efficiently than **1** (TOF of 24 h^{-1} in conditions similar to entry 2 of Table 1). Current work focuses on optimizing the steric and electronic properties at boron and phosphorous centers to obtain optimal catalytic activity. Computational studies to unveil the full reaction mechanism are also well underway.

Supporting Information

Synthesis and characterization of **1**, catalytic procedures and DFT details are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the National Sciences and Engineering Research Council of Canada (NSERC, Canada) and the Centre de Catalyse et Chimie Verte (Quebec). M.-A. C. and M.-A. L. would like to thank NSERC and FQRNT for scholarships. We would like to acknowledge W. Bi for the X-ray structure of **1** and R. Lafleur-Lambert with his help setting some catalytic experiments. LM is member of the Institut Universitaire de France. Cines and CALMIP are acknowledged for a generous grant of computing time. The Humboldt foundation is also acknowledged for financial support.

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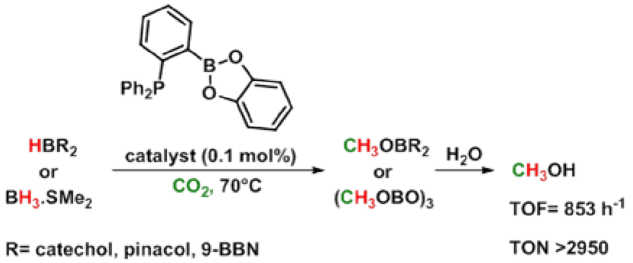
Ph2P
B
O
O
HBR2
or
BH3.SMe2
catalyst (0.1 mol%)
CO2, 70°C
CH3OBR2
or
(CH3OBO)3
H2O
CH3OH
TOF= 853 h-1
TON >2950
R= catechol, pinacol, 9-BBN