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Organocatalysts with carbon-centered activity for CO₂ reduction with boranes†

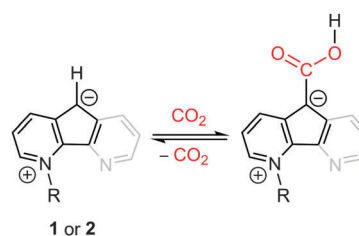
Yanxin Yang, Maotong Xu and Datong Song*

We report two organocatalysts for CO₂ hydroboration to methylborylethers, which upon hydrolysis can produce methanol. These organocatalysts feature carbon-centered reversible CO₂ binding, broad borane scopes, and high catalytic activities.

The use of fossil fuels has caused a drastic increase of CO₂ emissions over the past few decades.¹ While the increase in CO₂ level in the atmosphere raises serious environmental concerns, it also presents an opportunity for using CO₂ as a sustainable C₁ feedstock for chemical syntheses.² Many promising methods have been developed for the conversion of CO₂ to value-added chemicals, such as carbonates and derivatives, carboxylic acids and derivatives, formaldehyde, CO, alkanes, methylamines, and methanol.^{2,3} The catalytic reduction of CO₂ to methanol is particularly interesting as it converts the combustion product back to a liquid fuel. Three general routes have been reported for the catalytic conversion of CO₂ to methanol: hydrogenation,^{4,5} hydrosilylation,⁶ and hydroboration.⁷ A few transition metal⁷ and main group metal⁸ catalysts have been reported for the hydroboration of CO₂ into methylborylether, which upon hydrolysis produces methanol. The metal-free phosphine-borane frustrated Lewis pairs (FLPs)⁹ and a few borohydride species¹⁰ have also shown catalytic activity towards the same transformation. Most of the above catalysts are plagued with intrinsic air- and moisture-sensitivity. In 2014, Cantat and co-workers reported the air- and moisture-stable N-heterocycle-based catalysts that only contain carbon, hydrogen, and nitrogen. These catalysts feature nitrogen-centered activity for catalysis.¹¹ Unfortunately, these catalysts have limited borane scope, *i.e.*, 9-borabicyclo[3.3.1]nonane (9-BBN) only. Despite these recent advances in CO₂ reduction into methanol *via* catalytic hydroboration with heteroatom-centered reactivity, a catalyst with

carbon-centered reactivity is unknown for this transformation. It is worth pointing out that although N-heterocyclic carbenes (NHCs) are known to catalyze the hydrosilylation of CO₂ to methylsilylethers^{6a,b} and the methylation of amines using CO₂ as the carbon source,¹² the hydroboration of CO₂ into methylborylethers catalyzed by NHCs remains unknown.

Previously our group discovered the reversible CO₂ insertion into the C–H bond of the actor 4,5-diazafluorenyl ligand supported by spectator metal centers.¹³ To confirm the spectator role of the metal centers, we further demonstrated this new reactivity with a metal-free compound, *N*-methyl-4,5-diazafluorene, **1** (Scheme 1) by replacing spectator metal centers with a methyl group.^{13b} To probe what structural features are essential for this new type of CO₂ reactivity, we simplified the molecule from the three-ring system in **1** to a two-ring system in **2** (Scheme 1), because one of the pyridine moieties (color coated in gray) has no obvious role in CO₂ binding. Gratifyingly, **2** can indeed react with CO₂ reversibly by inserting CO₂ into the C–H bond (Scheme 1) on the C₅ ring. Both **1** and **2** bind with CO₂ at the reactive carbon center, which is reminiscent of CO₂-binding activity of NHCs.¹⁴ The carbon-centered CO₂-binding property of **1** and **2** led us to explore the catalytic activity of these compounds toward hydroboration of CO₂. The results are reported herein. To the best of our knowledge, the air- and moisture-stable and C/H/N-only compounds **1** and **2** are the first examples of carbon-centered catalysts for the hydroboration of CO₂ into methylborylethers.



Scheme 1 Reversible CO₂ binding by **1** (R = Me, with the gray portion) and **2** (R = *n*-Pr, without the gray portion).

Davenport Chemical Research Laboratories, Department of Chemistry,
University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6, Canada.
E-mail: dsong@chem.utoronto.ca

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Our initial tests showed that **1** could catalyze the hydroboration of CO₂ with 9-BBN and catecholborane (HBcat). For example, when a C₆D₅Br solution of **1** and 10 eq. of 9-BBN was heated at 70 °C overnight under 1 atm of ¹³CO₂, the major product ¹³CH₃OBBN was observed along with a small amount of ¹³CH₂(OBBN)₂ in the ¹H and ¹³C NMR spectra (see Fig. S16 and S17, ESI†). Similarly, when a C₆D₅Br solution of **1** and 30 eq. of HBcat was heated at 70 °C under 1 atm of ¹³CO₂ for 2 h, NMR experiments showed that ¹³CH₃OBBN was the only ¹³CO₂ reduction product (see Fig. S18 and S19, ESI†). These preliminary results encouraged us to test the catalytic performance of **1** further. A C₆D₅Br solution of **1** and 100 eq. of HBcat was exposed to 1.5 atm of CO₂ at 25 °C and the reaction was monitored with ¹H and ¹¹B NMR spectroscopy. The plot of TON vs. time for this reaction is shown in Fig. 1. The reaction started with a short induction period followed by fast catalysis. As HBcat was getting depleted toward the end of the reaction, the reaction rate was approaching 0. No induction period was

observed at 70 °C and the reaction profile consisted of two stages: fast catalysis and plateau. The TOFs at the fast catalysis stage of the reactions were extracted from the plot: 41 and 231 h⁻¹ for 25 °C and 70 °C reactions, respectively. Such TOFs put **1** amongst the most active organocatalysts for this transformation.

When a C₆D₅Br solution of **1** and 100 eq. of HBcat was exposed to 1.5 atm of CO₂ at 25 °C, CH₃OBBN was produced with a TON of 97 within 6 h (Table 1, entry 1). When the same reaction was carried out at 70 °C, the reaction reached completion within 2 h (Table 1, entry 2); to test whether the catalyst was still active after 100 turnovers, 21.5 h after the complete consumption of the first 100 eq. of HBcat, another 100 eq. of HBcat was added to the reaction mixture, which was then re-charged with 1.5 atm of CO₂ and reheated at 70 °C. The second batch of HBcat was consumed within 3 h to give an overall TON of 196 (Table 1, entry 3), indicating that catalyst **1** was still highly active.[§]

When 9-BBN was used as the reductant under the same conditions, the formations of CH₂(OBBN)₂ and CH₃OBBN were observed at 25 °C within 8 h with a total TON of 58 (Table 1, entry 4); if the same reaction was carried out at 70 °C, the TON reached 66 within 2 h (Table 1, entry 5) and again CH₂(OBBN)₂ and CH₃OBBN were both produced. The lower reaction rates in entries 4 and 5 compared to those in entries 1 and 2, respectively, could be attributed to the low solubility of 9-BBN. When a less reactive reductant pinacolborane (HBpin) was used, the catalytic reaction only gave 14 total turnovers in 48 h at 100 °C, yielding three reduction products HCOOBpin, CH₂(OBpin)₂ and CH₃OBpin (Table 1, entry 6). Using 100 eq. of BH₃·SMe₂ (with respect to catalyst **1**) as the reductant under 1.5 atm of CO₂ the reaction achieved a TON of 294 with BH₃ within 44 h at 25 °C to yield (CH₃OBO)₃ (Table 1, entry 7). Increasing the reaction temperature from 25 °C to 70 °C only improved the reaction rate by a factor of ~2 (Table 1, entry 8).

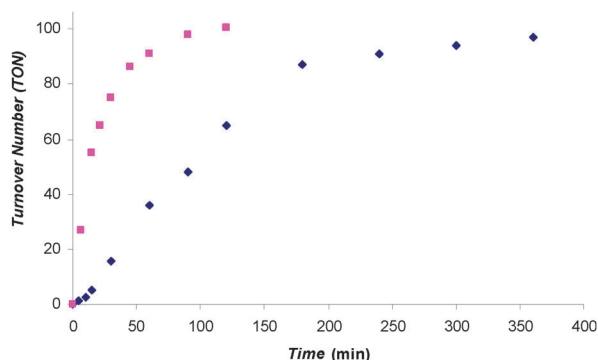


Fig. 1 TON vs. time plot for the formation of CH₃OBBN catalyzed by **1**. A C₆D₅Br solution of **1** and 100 eq. of HBcat was exposed to 1.5 atm CO₂ at 70 °C (■) and 25 °C (◆).

Table 1 Hydroboration of CO₂ by a variety of boranes^a

Entry	Cat.	Borane	Solvent	T (°C)	Time (h)	TON ^b from the formation of each product				Total TON ^b	Avg. TOF (h ⁻¹)
						HCO ₂ BR ₂	CH ₂ (OBR ₂) ₂	CH ₃ OBR ₂	(CH ₃ OBO) ₃		
1	1	HBcat	C ₆ D ₅ Br	25	6			97		97	16 (41) ^c
2	1	HBcat	C ₆ D ₅ Br	70	2			100		100	50 (231) ^c
3 ^d	1	HBcat	C ₆ D ₅ Br	70	2 + 3 ^e			196		196	39
4	1	9-BBN	C ₆ D ₅ Br	25	8		11	47		58	7.3
5	1	9-BBN	C ₆ D ₅ Br	70	2		16	51		67	34
6	1	HBpin	CDCl ₃	100	48	6.82	0.53	6.28		13.6	0.28
7	1	BH ₃ ·SMe ₂	C ₆ D ₆	25	44				294	294	6.7
8	1	BH ₃ ·SMe ₂	CDCl ₃	70	20.5				286 ^f	286	14.0
9	2	9-BBN	CDCl ₃	25	19		12.5	48.6		61	3.2
10	2	9-BBN	CDCl ₃	70	2		7.2	59		66.2	33
11	2	HBpin	CDCl ₃	90	46	1.6		73		74.6	1.6
12	2	HBcat	CDCl ₃	25	19			97		97	5.1
13	2	BH ₃ ·SMe ₂	CDCl ₃	25	7				298	298	42.6 (55.6) ^c

^a Reaction conditions: a Schlenk bomb was charged with 1.0 mg **1** or **2** and 100 eq. of borane, ~0.6 mL of a deuterated solvent, and 1.5 atm of CO₂. The internal standard, hexamethylbenzene was added to the reaction mixture upon completion. ^b TON is based on the number of C–H bonds formed in the reduced products per molecule of the catalyst, determined by ¹H NMR integration against the internal standard. ^c The number in parentheses is the TOF at the fast catalysis stage of the reaction. ^d The second 100 eq. of HBcat was added 21.5 h after the complete consumption of the first 100 eq. ^e The two numbers are the time required to consume the two batches of HBcat, respectively. ^f Control experiment (*i.e.*, same conditions except for the absence of the catalyst) for entry 8 showed 4.5% conversion of BH₃·SMe₂ to (CH₃OBO)₃, while all other entries have no background reactions.



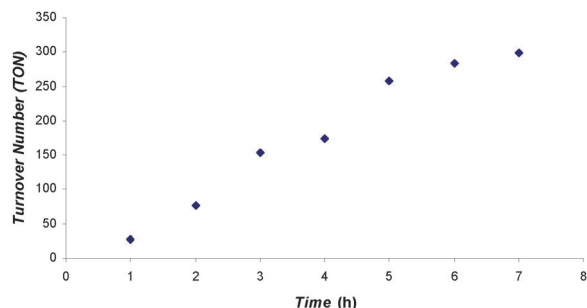


Fig. 2 TON vs. time plot for the formation of $(\text{CH}_3\text{OBO})_3$ catalyzed by **2**. A CDCl_3 solution of **2** and 100 eq. of $\text{BH}_3\cdot\text{SMe}_2$ was exposed to 1.5 atm of CO_2 at 25 °C.

Next, we tested the catalytic activity of **2**. When a CDCl_3 solution of **2** and 100 eq. of 9-BBN was exposed to 1.5 atm of CO_2 at 25 °C, $\text{CH}_2(\text{OBBN})_2$ and CH_3OBBN were produced with an overall TON of 61 within 19 h (Table 1, entry 9); the reaction is much slower than that catalyzed by **1**. When the same reaction was carried out at 70 °C, however, the reaction rate is comparable to that catalyzed by **1** at 70 °C, *i.e.*, the reaction reached 66 TON within 2 h (Table 1, entry 10). Compared to **1**, **2** showed a higher activity when HBpin was used as the reductant, *i.e.*, the reaction catalyzed by **2** gave CH_3OBpin as the dominant CO_2 reduction product with a TON of 75 in 46 h at 90 °C (Table 1, entry 11). In contrast, when HBcat was used as the reductant, catalyst **2** showed lower activity than **1** (Table 1, entry 12). We speculate that the difference in catalytic activity between **1** and **2** may originate partly from the preferred interactions between the catalyst and borane: the larger π -system in **1** interacts with the aromatic backbone of HBcat more strongly, while the longer aliphatic propyl chain and smaller π -system in **2** favor the aliphatic backbone of HBpin. Interestingly, **2** showed much higher catalytic activity than **1** when $\text{BH}_3\cdot\text{SMe}_2$ was used as the reductant, *i.e.*, complete conversion to $(\text{CH}_3\text{OBO})_3$ was observed in 7 h at 25 °C with a TON of 298 and average TOF of 42.6 h^{-1} (Table 1, entry 13). This reaction also has a short induction period at 25 °C (Fig. 2). A TOF of 56 h^{-1} at the fast catalysis stage was extracted from the plot of TON vs. time. Such TOFs make **2** one of the best organocatalysts for this transformation.

In summary, we have demonstrated compounds **1** and **2** not only bind CO_2 reversibly *via* the formal insertion of CO_2 into a C–H bond of the C_5 ring, but also catalyze the hydroboration of CO_2 to methylborylethers which upon hydrolysis can produce methanol. These air- and moisture-stable compounds that consist of only carbon, hydrogen, and nitrogen are the first catalysts with carbon-centered activity for the reduction of CO_2 to methylborylethers. These catalysts feature broad borane scope and their catalytic activities are comparable to the best organocatalysts with heteroatom-based activity. The mechanism of the catalytic reactions are currently being investigated *via* experimental and computational methods in our laboratory.

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Notes and references

‡ Compound **2** is an orange oil and can be synthesized using a modified literature procedure. Compared to **1**, whose solution is stable in air for several hours, the solution of **2** can be stored at –15 °C in air for weeks without significant change. Compound **2** is soluble in all common organic solvents. For the synthetic protocol of **2** and CO_2 binding experiments, see ESI.†

§ The slightly slower conversion of the second batch of HBcat was likely due to the inefficient mixing of the reactants caused by the large amount of solid produced in the reaction.

¶ The Schlenk bomb charged with all other reagents and solvents was immersed in liquid N_2 to freeze the solution; the headspace was then evacuated. The entire bomb was then immersed in a –70 °C dry ice-isopropanol bath to keep the solution frozen and cool the headspace. The bomb was then opened to 1 atm of CO_2 for 10 minutes to allow the temperature to equilibrate. Subsequently the bomb was sealed and allowed to warm to 25 °C to achieve ~1.5 atm pressure. Safety warning: if CO_2 gas was introduced below –78 °C, dry ice would condense in the reaction vessel and the final pressure becomes time-dependent and can no longer be calculated easily. Using our protocol with a low-melting solvent (*i.e.*, the solvent is not frozen at –70 °C), the final pressure is again time-dependent, because of the dramatically increased solubility of CO_2 at –70 °C. In both scenarios prolonged CO_2 exposure could cause serious explosions due to uncontrolled high pressures and make the results incomparable to others due to unknown CO_2 pressure.

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