

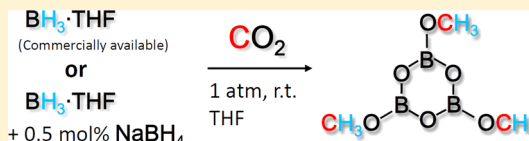
# Reduction of CO<sub>2</sub> to Trimethoxyboroxine with BH<sub>3</sub> in THF

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## Supporting Information

**ABSTRACT:** Commercially available THF solutions of BH<sub>3</sub>·THF, which contain 0.5 mol % of NaBH<sub>4</sub> as a stabilizing reagent for BH<sub>3</sub>·THF, react with 1 atm of CO<sub>2</sub> at room temperature to form trimethoxyboroxine, (MeOBO)<sub>3</sub>, in 87% yield after 12 h. Since no reaction took place in the absence of NaBH<sub>4</sub>, NaBH<sub>4</sub> was found to work as a promoter or catalyst for the reduction of CO<sub>2</sub> with BH<sub>3</sub> to the methoxy compound. A similar reaction using HCOONa in place of NaBH<sub>4</sub> also gave (MeOBO)<sub>3</sub> in comparable yield.



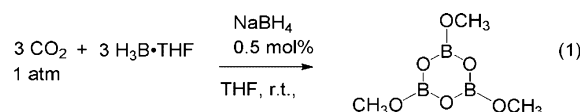
A dramatic increase in global fuel consumption and the resulting emissions of enormous quantities of CO<sub>2</sub> are contemporary energy and environmental issues. Since the utilization of CO<sub>2</sub> as the C<sub>1</sub> building block for fuels and chemicals is one of the most promising strategies to solve both issues, reduction of CO<sub>2</sub> has been extensively investigated.<sup>1</sup> Most of these studies are on the formation of formic acid, which is obtained with excellent turnover numbers of up to 222 000 using half-sandwich iridium(III) complexes reported by Himeda et al. and 3 500 000 using an iridium(III) trihydride pincer complex by Nozaki et al.<sup>2</sup> On the other hand, a relatively limited number of studies have been reported for further reduction to give methoxy products. Recent examples employ nickel and ruthenium complexes as catalysts for hydroboration reactions.<sup>3</sup> In addition to these transition-metal-catalyzed CO<sub>2</sub> reductions, transition-metal-free systems such as frustrated Lewis acid–base pair systems have also attracted recent interest.<sup>4</sup> Another notable example using an organic catalyst is an ambiphilic phosphine–borane system reported by Fontaine.<sup>5</sup> They demonstrated that not only catecholborane, which has been frequently used as the reducing reagent for CO<sub>2</sub>, but also BH<sub>3</sub> are excellent reagents to afford methoxy derivatives.

In the course of our study on the transition-metal-catalyzed CO<sub>2</sub> reduction with BH<sub>3</sub>, we discovered a simple and very effective method for CO<sub>2</sub> reduction to a methoxy group using only a commercially available BH<sub>3</sub>·THF solution or a purified BH<sub>3</sub>·THF solution in the presence of a catalytic amount of NaBH<sub>4</sub>. The reactions do not require any sophisticated additives such as transition-metal catalysts or organocatalysts.<sup>6</sup> Here, we report the reaction conditions and discuss the reaction mechanisms.

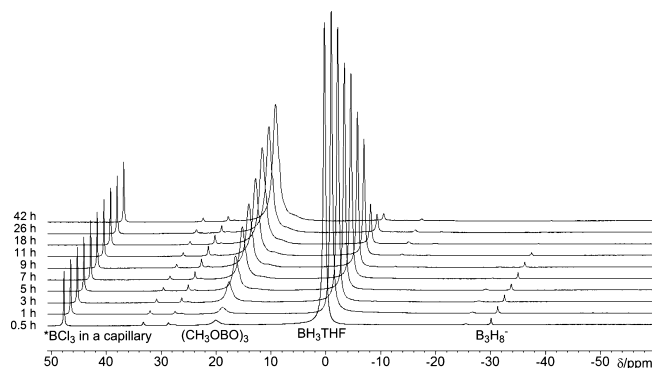
To the best of our knowledge, a reaction between CO<sub>2</sub> and BH<sub>3</sub>·THF in THF without any additives has not been reported. We confirmed that CO<sub>2</sub> at ambient temperature and pressure did not react with a “purified” BH<sub>3</sub>·THF solution, which was prepared by the trap-to-trap technique from a commercially available THF solution of BH<sub>3</sub>·THF. The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of the solution kept under a CO<sub>2</sub> atmosphere for 6 h

showed a major <sup>11</sup>B{<sup>1</sup>H} NMR signal assigned to the starting BH<sub>3</sub>·THF at −0.4 ppm.

On the other hand, in the presence of a catalyst, there are several reports in which BH<sub>3</sub>·THF was used as the reducing reagent for CO<sub>2</sub>. To our surprise, however, when the commercially available BH<sub>3</sub>·THF solution (ca. 1 M in THF) was used as received without purification, the BH<sub>3</sub>·THF solution reacted with CO<sub>2</sub> to give trimethoxyboroxine, (CH<sub>3</sub>OBO)<sub>3</sub> (eq 1), which was characterized by a <sup>11</sup>B{<sup>1</sup>H}



NMR signal at 19.3 ppm and a <sup>13</sup>C{<sup>1</sup>H} NMR signal at 51.6 ppm assigned to the methoxy carbon.<sup>3i,5</sup> Monitoring of the reaction mixture with <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopy showed a decrease of BH<sub>3</sub>·THF and the concomitant increase of (CH<sub>3</sub>OBO)<sub>3</sub> as shown in Figure 1. After 12 h, the hydrolysis



**Figure 1.** Stack plot of <sup>11</sup>B{<sup>1</sup>H} NMR spectra for the reaction of a commercially available BH<sub>3</sub>·THF solution with 1 atm of CO<sub>2</sub> at rt.

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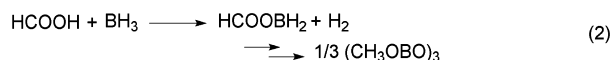
of the reaction mixture gave MeOH in 87% yield against the starting  $\text{BH}_3\cdot\text{THF}$ . The reaction was further examined using  $^{13}\text{CO}_2$ , which enabled more direct observation of the reaction products using  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. The spectrum recorded after the reaction showed only two signals, at 125.8 and 51.6 ppm, in addition to those of THF. These signals were assigned to starting  $^{13}\text{CO}_2$  and  $(^{13}\text{CH}_3\text{OBO})_3$  produced, respectively. Without proton decoupling, the latter signal was split into a quartet due to the coupling with three hydrogens, proving it was a methoxy carbon.

Commercially available  $\text{BH}_3\cdot\text{THF}$  contains <0.5 mol % of  $\text{NaBH}_4$  as a stabilizing reagent. It is known that  $\text{BH}_3\cdot\text{THF}$  in THF gradually decomposes through a ring-opening reaction of a THF molecule to form  $^t\text{BuOBH}_2$  when the solution is stored above 0 °C.<sup>7</sup> The  $^t\text{BuOBH}_2$  thus formed undergoes a redistribution reaction to give a mixture of  $(^t\text{BuO})_2\text{BH}$ ,  $(^t\text{BuO})_3\text{B}$ , and  $\text{BH}_3$ .<sup>8</sup> A small amount of  $\text{NaBH}_4$  is used to prevent the formation of  $^t\text{BuOBH}_2$ .<sup>7d</sup> The remarkably different reactivity against  $\text{CO}_2$  between the purified and commercially available  $\text{BH}_3\cdot\text{THF}$  suggests that  $\text{NaBH}_4$  in the latter solution plays an important role in promoting the reduction of  $\text{CO}_2$ . To confirm the role of  $\text{NaBH}_4$ , a catalytic amount (1.0 mol %) of  $\text{NaBH}_4$  was added to the purified  $\text{BH}_3\cdot\text{THF}$  solution, and under the same reaction conditions, the mixture gave  $(\text{CH}_3\text{OBO})_3$  in 83% yield, which is comparable to that of the commercially available  $\text{BH}_3\cdot\text{THF}$ .

To examine the hydroborate species in the  $\text{BH}_3\cdot\text{THF}$  solution, both the commercial  $\text{BH}_3\cdot\text{THF}$  solution and the  $\text{BH}_3\cdot\text{THF}$  solution mixed with 1.0 mol % of  $\text{NaBH}_4$  after trap-to-trap purification were checked using  $^{11}\text{B}$  NMR spectroscopy. The former solution was found to contain  $\text{B}_3\text{H}_8^-$  having a signal at  $-30.1$  ppm that splits into a septet when the spectrum was recorded in nondecoupled mode, as shown in Figure S6.<sup>9</sup> Similarly,  $\text{NaBH}_4$  added to the purified  $\text{BH}_3\cdot\text{THF}$  solution was not observed. Instead, a broad signal at  $-26$  ppm was observed, which could be assigned to  $\text{B}_2\text{H}_7^-$ .<sup>10</sup> Since both  $\text{B}_3\text{H}_8^-$  and  $\text{B}_2\text{H}_7^-$  are reported to be in an equilibrium with  $\text{BH}_4^-$ , the reaction of  $\text{BH}_4^-$  with  $\text{CO}_2$  is of interest.<sup>9,10</sup>

There are several relevant reactions of a  $\text{BH}_4^-$  anion with  $\text{CO}_2$  in the literature. The first one appeared in the 1950s. Heller et al. examined the reaction of radioactive  $^{14}\text{CO}_2$  with  $\text{LiBH}_4$  in ether and found the formation of  $\text{HCOOLi}$  and  $1/2\text{B}_2\text{H}_6$  as well as a small amount of MeOH.<sup>11</sup> Pearson et al. reported the formation of methoxy and formate compounds from the reaction of  $\text{CO}_2$  with  $\text{NaBH}_4$ , but they did not spectroscopically characterize the products.<sup>12</sup> Thirty years later, La Monica et al. carried out the reduction of  $\text{CO}_2$  with free  $\text{BH}_4^-$ , which was dissociated from tetrahydroborate–metal complexes formulated as (diimine)( $\text{Ph}_3\text{P}$ ) $\text{Cu}(\text{BH}_4)$  (diimine = 1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline).<sup>13</sup> The reaction gave  $(\text{HCOO})_2\text{BH}_2^-$  and  $(\text{HCOO})_3\text{BH}^-$ , which were spectroscopically identified. The latter species was thermodynamically unstable and obtained only when the reaction was carried out at  $-50$  °C. Otherwise, it decomposed to  $(\text{HCOO})_2\text{BH}_2^-$  and  $\text{CO}_2$ .

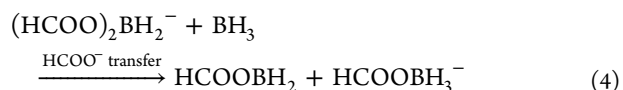
On the other hand, the formation of trimethoxyboroxine was reported by Brown, who obtained it by the reaction of formic acid ( $\text{HCOOH}$ ) with  $\text{BH}_3\cdot\text{THF}$  at 0 °C in THF.<sup>14</sup> The reaction gave  $\text{HCOOBH}_2$  as an intermediate with the evolution of dihydrogen.  $\text{HCOOBH}_2$  thus formed reacted further and eventually formed trimethoxyboroxine in good yield (eq 2). Brown also reported the reaction of carbon monoxide ( $\text{CO}$ ) with  $\text{BH}_3\cdot\text{THF}$ . Interestingly, the reaction gave a simple



donor–acceptor adduct of  $\text{BH}_3\cdot\text{CO}$ , but in the presence of a catalytic amount of  $\text{NaBH}_4$ , the reaction gave trimethylboroxine,  $(\text{CH}_3\text{BO})_3$ , which is the methyl version of the present  $\text{CO}_2$  reduction forming trimethoxyboroxine,  $(\text{CH}_3\text{OBO})_3$ .<sup>15</sup>

More recent transition-metal-free systems for the activation of  $\text{CO}_2$  commonly use strong Lewis bases, such as N-heterocyclic carbenes and  $\text{P}^t\text{Bu}_3$ .<sup>16</sup> These bases attack the carbon center of  $\text{CO}_2$  to make the oxygen atoms more nucleophilic, leading to a stronger interaction with a Lewis acid such as  $\text{BAr}_3$  and hydrosilane. In the present case,  $\text{BH}_4^-$  works as a Lewis base to activate  $\text{CO}_2$ . Thus, the activated  $\text{CO}_2$  is reduced by  $\text{BH}_3$  to give the initial reduction product of  $\text{HCOOBH}_2$ , which transforms to the final product of trimethoxyboroxine as reported by Brown.<sup>14</sup>

In the present reaction, since the  $\text{BH}_4^-$  itself can directly reduce  $\text{CO}_2$  to form  $\text{HCOOBH}_3^-$ , another catalytic mechanism is also possible as shown in eqs 3 and 4. The initial step is the formation of  $\text{HCOOBH}_3^-$ , which further reacts with  $\text{CO}_2$  to give  $(\text{HCOO})_2\text{BH}_2^-$  as in eq 3. La Monica et al. observed that  $\text{HCOO}^-$  dissociates from  $(\text{HCOO})_2\text{BH}_2^-$ . Since further reaction with  $\text{CO}_2$  does not proceed at ambient temperature,  $(\text{HCOO})_2\text{BH}_2^-$  reacts with  $\text{BH}_3$ , which can then abstract a  $\text{HCOO}^-$  group from  $(\text{HCOO})_2\text{BH}_2^-$  to form  $\text{HCOOBH}_3^-$  and  $\text{HCOOBH}_2$  as in eq 4. The former  $\text{HCOOBH}_3^-$  returns to the catalytic cycle, while the latter turns into the final product. In this mechanism, it is considered that a catalytic amount of  $\text{HCOO}^-$  can also initiate the catalytic cycle. In fact, addition of 1.0 mol % of  $\text{HCOONa}$  in place of  $\text{NaBH}_4$  to the  $\text{BH}_3\cdot\text{THF}$  solution led to the similar efficient transformation of  $\text{CO}_2$  into trimethoxyboroxine in 78% yield. The sodium cation commonly contained in both  $\text{NaBH}_4$  and  $\text{HCOONa}$  did not contribute to the  $\text{CO}_2$  reduction, since the reduction did not proceed at all in the presence of sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate.



In summary,  $\text{BH}_3\cdot\text{THF}$  with a catalytic amount of  $\text{NaBH}_4$  or  $\text{HCOONa}$  efficiently reduces  $\text{CO}_2$  to trimethoxyboroxine under ambient conditions. This reaction is simple and very effective for the synthesis of trimethoxyboroxine, which is a useful material as an electrolyte of lithium-ion batteries and a flame retardant.

## EXPERIMENTAL SECTION

**General Comments.** All manipulations of the reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques.  $\text{BH}_3\cdot\text{THF}$  solutions were obtained from Aldrich Inc. or Tokyo Kasei Co. and purified by trap-to-trap transfer in vacuo. The concentration of  $\text{BH}_3\cdot\text{THF}$  was determined by a titration of boric acid after hydrolysis of  $\text{BH}_3$ .  $\text{CO}_2$  (99.995%) and  $^{13}\text{CO}_2$  were purchased from NIPPON EKITAN Co. and Taiyo Nippon Sanso, respectively. Other reagents were used as received. NMR spectra were recorded on a Jeol LA-300 spectrometer.  $^{13}\text{C}$  NMR chemical shifts were reported relative to  $\text{Me}_4\text{Si}$  and were determined by reference to the solvent peaks.  $^{11}\text{B}$  NMR chemical shifts were reported relative to  $\text{BF}_3\cdot\text{OEt}_2$ .

**Reaction of Commercial  $\text{BH}_3\cdot\text{THF}$ .** Under an atmosphere of dry  $\text{CO}_2$ , a Schlenk tube was charged with commercial  $\text{BH}_3\cdot\text{THF}$  (Tokyo

Chemical Industry, 0.911 M in THF, 4.0 mL) that contained  $\text{NaBH}_4$  (0.5 mol %) as a stabilizing reagent. After the THF solution was stirred 12 h,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of the solution were recorded. The yield of  $(\text{MeOBO})_3$  was 87%, which was determined with the GC analysis of MeOH formed by hydrolysis of  $(\text{MeOBO})_3$ .  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.6 MHz, 297 K, THF):  $\delta$  51.6 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96.4 MHz, 297 K, THF):  $\delta$  19.2 (s).

**Monitoring the Reaction of Commercial  $\text{BH}_3\cdot\text{THF}$ .** Under an atmosphere of  $\text{CO}_2$ , an NMR tube was charged with commercial  $\text{BH}_3\cdot\text{THF}$  (Tokyo Chemical Industry, 0.911 M in THF, 0.5 mL), and then a sealed capillary containing  $\text{BCl}_3$  was placed in the NMR tube to calibrate the chemical shifts of the spectra for 2 days.

**Reaction of Purified  $\text{BH}_3\cdot\text{THF}$ .** Under an atmosphere of dry  $\text{CO}_2$ , a Schlenk tube was charged with  $\text{BH}_3\cdot\text{THF}$  (0.993 M in THF, 2.8 mL), which was purified by trap-to-trap transfer. After the THF solution was stirred 12 h, an  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of the solution was recorded, showing a signal at  $-0.5$  ppm assigned to  $\text{BH}_3\cdot\text{THF}$ .

**Reaction of Purified  $\text{BH}_3\cdot\text{THF}$  in the Presence of  $\text{NaBH}_4$ .** Under an atmosphere of dry  $\text{CO}_2$ , a Schlenk tube was charged with  $\text{NaBH}_4$  (1.52 mg) and  $\text{BH}_3\cdot\text{THF}$  (0.893 M in THF, 4.5 mL), which was purified by trap-to-trap transfer. After the THF solution was stirred 12 h,  $(\text{MeOBO})_3$  was obtained in 83% yield.

**Reaction of Purified  $\text{BH}_3\cdot\text{THF}$  in the Presence of  $\text{HCOONa}$ .** Under an atmosphere of dry  $\text{CO}_2$ , a Schlenk tube was charged with  $\text{HCOONa}$  (3.24 mg) and  $\text{BH}_3\cdot\text{THF}$  (0.893 M in THF, 5.34 mL), which was purified by trap-to-trap transfer. After the THF solution was stirred 12 h,  $(\text{MeOBO})_3$  was obtained in 79% yield.

**Reaction of Commercial  $\text{BH}_3\cdot\text{THF}$  with  $^{13}\text{CO}_2$ .** Under an atmosphere of  $\text{N}_2$ , an NMR tube with a J Young valve was charged with commercial  $\text{BH}_3\cdot\text{THF}$  (Tokyo Chemical Industry, 0.911 M in THF, 0.5 mL), and then the headspace gas was replaced with  $^{13}\text{CO}_2$ . After 2.5 h, a  $^{13}\text{C}$  NMR spectrum of the solution was recorded.  $^{13}\text{C}$  NMR (75.6 MHz, 297 K, THF):  $\delta$  26.3 (t, THF), 51.6 (q,  $(\text{MeOBO})_3$ ), 68.3 (t, THF), 125.8 (s,  $\text{CO}_2$ ).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional experimental data details including NMR data. 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 interest.

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