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Reduction of CO_2 to Trimethoxyboroxine with BH_3 in THF

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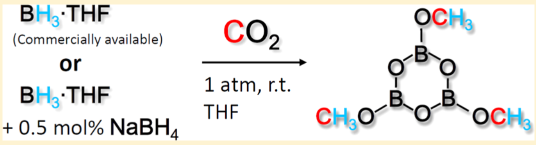
Supporting Information

ABSTRACT: Commercially available THF solutions of $BH_3{\cdot}THF$, which contain 0.5 mol % of $NaBH_4$ as a stabilizing reagent for $BH_3{\cdot}THF$, react with 1 atm of CO_2 at room temperature to form trimethoxyboroxine, $(MeOBO)_3$, in 87% yield after 12 h. Since no reaction took place in the absence of $NaBH_4$, $NaBH_4$ was found to work as a promoter or catalyst for the reduction of CO_2 with BH_3 to the methoxy compound. A similar reaction using HCOONa in place of $NaBH_4$ also gave $(MeOBO)_3$ in comparable yield.

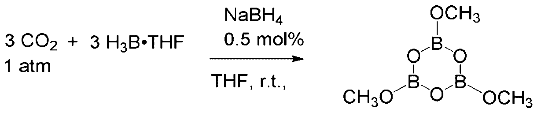


A dramatic increase in global fuel consumption and the resulting emissions of enormous quantities of CO_2 are contemporary energy and environmental issues. Since the utilization of CO_2 as the C_1 building block for fuels and chemicals is one of the most promising strategies to solve both issues, reduction of CO_2 has been extensively investigated.[1] 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.[2] 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.[3] In addition to these transition-metal-catalyzed CO_2 reductions, transition-metal-free systems such as frustrated Lewis acid−base pair systems have also attracted recent interest.[4] Another notable example using an organic catalyst is an ambiphilic phosphine−borane system reported by Fontaine.[5] They demonstrated that not only catecholborane, which has been frequently used as the reducing reagent for CO_2, but also BH_3 are excellent reagents to afford methoxy derivatives.

In the course of our study on the transition-metal-catalyzed CO_2 reduction with BH_3, we discovered a simple and very effective method for CO_2 reduction to a methoxy group using only a commercially available $BH_3{\cdot}THF$ solution or a purified $BH_3{\cdot}THF$ solution in the presence of a catalytic amount of $NaBH_4$. The reactions do not require any sophisticated additives such as transition-metal catalysts or organocatalysts.[6] Here, we report the reaction conditions and discuss the reaction mechanisms.

To the best of our knowledge, a reaction between CO_2 and $BH_3{\cdot}THF$ in THF without any additives has not been reported. We confirmed that CO_2 at ambient temperature and pressure did not react with a "purified" $BH_3{\cdot}THF$ solution, which was prepared by the trap-to-trap technique from a commercially available THF solution of $BH_3{\cdot}THF$. The $^{11}B\{^1H\}$ NMR spectrum of the solution kept under a CO_2 atmosphere for 6 h showed a major $^{11}B\{^1H\}$ NMR signal assigned to the starting $BH_3{\cdot}THF$ at −0.4 ppm.

On the other hand, in the presence of a catalyst, there are several reports in which $BH_3{\cdot}THF$ was used as the reducing reagent for CO_2. To our surprise, however, when the commercially available $BH_3{\cdot}THF$ solution (ca. 1 M in THF) was used as received without purification, the $BH_3{\cdot}THF$ solution reacted with CO_2 to give trimethoxyboroxine, $(CH_3OBO)_3$ (eq 1), which was characterized by a $^{11}B\{^1H\}$



(1)

NMR signal at 19.3 ppm and a $^{13}C\{^1H\}$ NMR signal at 51.6 ppm assigned to the methoxy carbon.[3i,5] Monitoring of the reaction mixture with $^{11}B\{^1H\}$ NMR spectroscopy showed a decrease of $BH_3{\cdot}THF$ and the concomitant increase of $(CH_3OBO)_3$ as shown in Figure 1. After 12 h, the hydrolysis

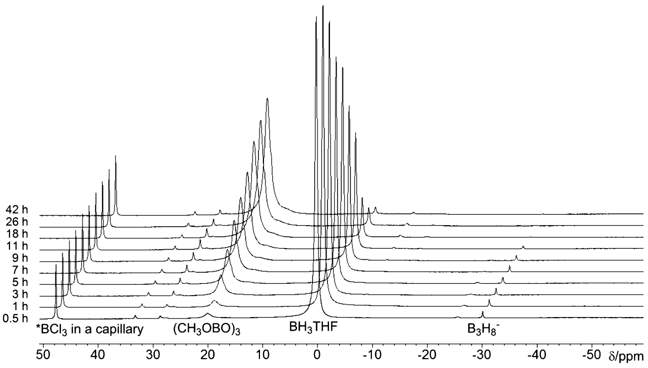


Figure 1. Stack plot of $^{11}B\{^1H\}$ NMR spectra for the reaction of a commercially available $BH_3{\cdot}THF$ solution with 1 atm of CO_2 at rt.

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of the reaction mixture gave MeOH in 87% yield against the starting BH_3·THF. The reaction was further examined using $^{13}CO_2$, which enabled more direct observation of the reaction products using $^{13}C\{^1H\}$ 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 $^{13}CO_2$ and $(^{13}CH_3OBO)_3$ 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 BH_3·THF contains <0.5 mol % of $NaBH_4$ as a stabilizing reagent. It is known that BH_3·THF in THF gradually decomposes through a ring-opening reaction of a THF molecule to form $^nBuOBH_2$ when the solution is stored above 0 °C.[7] The $^nBuOBH_2$ thus formed undergoes a redistribution reaction to give a mixture of $(^nBuO)_2BH$, $(^nBuO)_3B$, and BH_3.[8] A small amount of $NaBH_4$ is used to prevent the formation of $^nBuOBH_2$.[7d] The remarkably different reactivity against CO_2 between the purified and commercially available BH_3·THF suggests that $NaBH_4$ in the latter solution plays an important role in promoting the reduction of CO_2. To confirm the role of $NaBH_4$, a catalytic amount (1.0 mol %) of $NaBH_4$ was added to the purified BH_3·THF solution, and under the same reaction conditions, the mixture gave $(CH_3OBO)_3$ in 83% yield, which is comparable to that of the commercially available BH_3·THF.

To examine the hydroborate species in the BH_3·THF solution, both the commercial BH_3·THF solution and the BH_3·THF solution mixed with 1.0 mol % of $NaBH_4$ after trap-to-trap purification were checked using ^{11}B NMR spectroscopy. The former solution was found to contain $B_3H_8^-$ 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.[9] Similarly, $NaBH_4$ added to the purified BH_3·THF solution was not observed. Instead, a broad signal at −26 ppm was observed, which could be assigned to $B_2H_7^-$.[10] Since both $B_3H_8^-$ and $B_2H_7^-$ are reported to be in an equilibrium with BH_4^-, the reaction of BH_4^- with CO_2 is of interest.[9,10]

There are several relevant reactions of a BH_4^- anion with CO_2 in the literature. The first one appeared in the 1950s. Heller et al. examined the reaction of radioactive $^{14}CO_2$ with $LiBH_4$ in ether and found the formation of HCOOLi and $^1/_2B_2H_6$ as well as a small amount of MeOH.[11] Pearson et al. reported the formation of methoxy and formate compounds from the reaction of CO_2 with $NaBH_4$, but they did not spectroscopically characterize the products.[12] Thirty years later, La Monica et al. carried out the reduction of CO_2 with free BH_4^-, which was dissociated from tetrahydroborate−metal complexes formulated as $(diimine)(Ph_3P)Cu(BH_4)$ (diimine = 1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline).[13] The reaction gave $(HCOO)_2BH_2^-$ and $(HCOO)_3BH^-$, 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 $(HCOO)_2BH_2^-$ and CO_2.

On the other hand, the formation of trimethoxyboroxine was reported by Brown, who obtained it by the reaction of formic acid (HCOOH) with BH_3·THF at 0 °C in THF.[14] The reaction gave $HCOOBH_2$ as an intermediate with the evolution of dihydrogen. $HCOOBH_2$ thus formed reacted further and eventually formed trimethoxyboroxine in good yield (eq 2). Brown also reported the reaction of carbon monoxide (CO) with BH_3·THF. Interestingly, the reaction gave a simple donor−acceptor adduct of BH_3·CO, but in the presence of a catalytic amount of $NaBH_4$, the reaction gave tri*methyl*boroxine, $(CH_3BO)_3$, which is the methyl version of the present CO_2 reduction forming trimethoxyboroxine, $(CH_3OBO)_3$.[15]

$$HCOOH + BH_3 \longrightarrow HCOOBH_2 + H_2 \rightrightarrows \tfrac{1}{3}\,(CH_3OBO)_3 \tag{2}$$

More recent transition-metal-free systems for the activation of CO_2 commonly use strong Lewis bases, such as N-heterocyclic carbenes and P^tBu_3.[16] These bases attack the carbon center of CO_2 to make the oxygen atoms more nucleophilic, leading to a stronger interaction with a Lewis acid such as BAr_3 and hydrosilane. In the present case, BH_4^- works as a Lewis base to activate CO_2. Thus, the activated CO_2 is reduced by BH_3 to give the initial reduction product of $HCOOBH_2$, which transforms to the final product of trimethoxyboroxine as reported by Brown.[14]

In the present reaction, since the BH_4^- itself can directly reduce CO_2 to form $HCOOBH_3^-$, another catalytic mechanism is also possible as shown in eqs 3 and 4. The initial step is the formation of $HCOOBH_3^-$, which further reacts with CO_2 to give $(HCOO)_2BH_2^-$ as in eq 3. La Monica et al. observed that $HCOO^-$ dissociates from $(HCOO)_2BH_2^-$. Since further reaction with CO_2 does not proceed at ambient temperature, $(HCOO)_2BH_2^-$ reacts with BH_3, which can then abstract a $HCOO^-$ group from $(HCOO)_2BH_2^-$ to form $HCOOBH_3^-$ and $HCOOBH_2$ as in eq 4. The former $HCOOBH_3^-$ returns to the catalytic cycle, while the latter turns into the final product. In this mechanism, it is considered that a catalytic amount of $HCOO^-$ can also initiate the catalytic cycle. In fact, addition of 1.0 mol % of HCOONa in place of $NaBH_4$ to the BH_3·THF solution led to the similar efficient transformation of CO_2 into trimethoxyboroxine in 78% yield. The sodium cation commonly contained in both $NaBH_4$ and HCOONa did not contribute to the CO_2 reduction, since the reduction did not proceed at all in the presence of sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate.

$$HCOOBH_3^- + CO_2 \rightarrow (HCOO)_2BH_2^- \tag{3}$$

$$(HCOO)_2BH_2^- + BH_3 \xrightarrow{\text{HCOO}^- \text{ transfer}} HCOOBH_2 + HCOOBH_3^- \tag{4}$$

In summary, BH_3·THF with a catalytic amount of $NaBH_4$ or HCOONa efficiently reduces 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. BH_3·THF solutions were obtained from Aldrich Inc. or Tokyo Kasei Co. and purified by trap-to-trap transfer in vacuo. The concentration of BH_3·THF was determined by a titration of boric acid after hydrolysis of BH_3. CO_2 (99.995%) and $^{13}CO_2$ 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}C NMR chemical shifts were reported relative to Me_4Si and were determined by reference to the solvent peaks. ^{11}B NMR chemical shifts were reported relative to BF_3·OEt_2.

Reaction of Commercial BH_3·THF. Under an atmosphere of dry CO_2, a Schlenk tube was charged with commercial BH_3·THF (Tokyo

Chemical Industry, 0.911 M in THF, 4.0 mL) that contained $NaBH_4$ (0.5 mol %) as a stabilizing reagent. After the THF solution was stirred 12 h, $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra of the solution were recorded. The yield of $(MeOBO)_3$ was 87%, which was determined with the GC analysis of MeOH formed by hydrolysis of $(MeOBO)_3$. $^{13}C\{^1H\}$ NMR (75.6 MHz, 297 K, THF): δ 51.6 (s). $^{11}B\{^1H\}$ NMR (96.4 MHz, 297 K, THF): δ 19.2 (s).

Monitoring the Reaction of Commercial BH_3·THF. Under an atmosphere of CO_2, an NMR tube was charged with commercial BH_3·THF (Tokyo Chemical Industry, 0.911 M in THF, 0.5 mL), and then a sealed capillary containing BCl_3 was placed in the NMR tube to calibrate the chemical shifts of the spectra for 2 days.

Reaction of Purified BH_3·THF. Under an atmosphere of dry CO_2, a Schlenk tube was charged with BH_3·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 $^{11}B\{^1H\}$ NMR spectrum of the solution was recorded, showing a signal at −0.5 ppm assigned to BH_3·THF.

Reaction of Purified BH_3·THF in the Presence of $NaBH_4$. Under an atmosphere of dry CO_2, a Schlenk tube was charged with $NaBH_4$ (1.52 mg) and BH_3·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, $(MeOBO)_3$ was obtained in 83% yield.

Reaction of Purified BH_3·THF in the Presence of HCOONa. Under an atmosphere of dry CO_2, a Schlenk tube was charged with HCOONa (3.24 mg) and BH_3·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, $(MeOBO)_3$ was obtained in 79% yield.

Reaction of Commercial BH_3·THF with $^{13}CO_2$. Under an atmosphere of N_2, an NMR tube with a J Young valve was charged with commercial BH_3·THF (Tokyo Chemical Industry, 0.911 M in THF, 0.5 mL), and then the headspace gas was replaced with $^{13}CO_2$. After 2.5 h, a ^{13}C NMR spectrum of the solution was recorded. ^{13}C NMR (75.6 MHz, 297 K, THF): δ 26.3 (t, THF), 51.6 (q, $(MeOBO)_3$), 68.3 (t, THF), 125.8 (s, 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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