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Alkaline Earth-Catalyzed CO₂ Hydroboration into Acetal Derivatives Leading to C-S Bond Formation.

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ABSTRACT: The use of Mg and Ca hydride catalysts for the 4e- reduction of CO₂ is reported. Borabicyclo[3.3.1]nonane (9-BBN) and dicyclohexylborane (HBCy₂) - as reductants - led to the generation of the corresponding bis(boryl)acetal (BBA) which in situ reacted with thiol to afford new borylated hemithioacetal compounds (R₂BOCH₂SR) under mild neutral conditions. These hemithioacetals were then converted into dithioacetal (RSCH₂SR) with the addition of a second equivalent of thiol under acidic activation, or amino-methyl sulfide (RSCH₂NR₂) upon reaction with secondary amine.

INTRODUCTION

Earth abundant Mg- and Ca-based complexes **A-E** have been shown to catalyze CO₂ hydroboration with three equivalents of pinacolborane (HBpin) into the corresponding methoxyborane (pinBOCH₃) and boroxane (pinBOBpin) (Scheme 1a).¹⁻⁵ In more detail, in 2014 it was demonstrated that 10 mol% of Mg- and Ca-based hydride complexes **A** and **B** catalyzed this transformation within 6 and 4 days, respectively, at 60 °C,⁴ while the simpler Mg borohydride complex **C** (2016)³ and MgBu₂ **D** (2019)² catalyzed this reaction within 3 h at 25 °C and 16 h at 95 °C, respectively, with 10 mol% catalyst loading. Finally in 2020, it was reported that the Mg(I) dimer complex **E** catalyzed the same transformation in 15 h at 100 °C in 96 % in situ yield with 5 mol% catalyst loading.¹ Overall, only 5 Ae-based complexes have been probed as catalysts in CO₂ hydroboration. HBpin was used as reductant, leading exclusively to the 6e- reduction product. There is room for improving the efficiency of the catalytic conversion since the maximum TON and TOF values of 19 and 1.3 h⁻¹, respectively, were reported at 100 °C with catalyst **E**. Moreover, there is no example of Mg- or Ca-catalyzed hydroboration of CO₂ to the 2e- or to the 4e- reduction products.

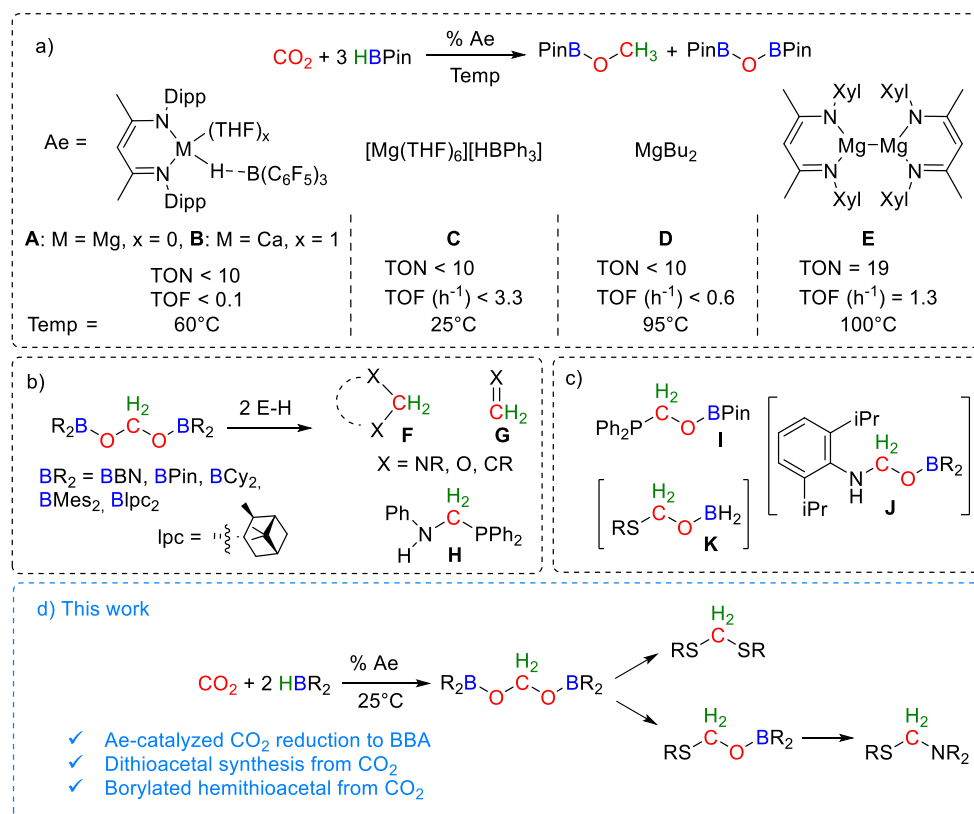
4e- reduction of CO₂ is an appealing reduction stage because the obtained product is usually a very reactive compound.⁶ While this is also a challenging reduction stage to realize, the formation of bis(boryl)acetal (BBA) compounds via double CO₂ hydroboration was an efficient way to stabilize the 4e- reduction level.⁷⁻¹⁰ Once generated, the resulting BBA^{BBN},¹¹ BBA^{pin},¹² BBA^{Mes}, BBA^{lpc}, and BBA^{Cy} were successfully used as C₁ source,¹³ as versatile methylene transferring agents. Their reaction with E-H (E = OR, NR₂, PPh₂, CR₃) co-reactants gave rise to new H₂C-N, H₂C-C, H₂C-O and H₂C-P bonds to form a variety of compounds (**F-H**, Scheme 1b). BBA^{BBN} and BBA^{Mes} were also used as C_n sources.¹⁴⁻¹⁶

The mechanism involving the condensation reaction of BBA with E-H functions remains unclear as to whether two sequential additions of the E-H bond on the O-CH₂ bonds occur or if formaldehyde is simply released initially and then condensed. Compound **I** (Scheme 1c), generated from the reaction of BBA^{Pin} with a secondary phosphine, was characterized by NMR as an intermediate during the formation of compound **H**, in line with the sequential pathway without release of formaldehyde.¹² A related intermediate **J** was proposed in the reaction of various BBA with aniline, based on kinetic analysis and theoretical investigations but was never observed.¹³ Furthermore, the related intermediate **K** was proposed in CO₂ reductive functionalization but neither observed nor explored by theoretical means in C-S bond formation.¹⁷⁻¹⁸ In this latter case, it should be noticed that BBA was not proposed as an intermediate.

Because organosulfur compounds are important substances in various fields, their generation from CO₂ is of interest. On the one hand, a variety of dithioacetal compounds (RS-CH₂-SR) were generated from CO₂ and a NaBH₄/I₂ system.¹⁷⁻¹⁸ On the other hand, related dithioacetal were also synthesized from CO₂ hydrosilylation via the formation of bis(silyl)acetal (BSA) and subsequent formaldehyde release in the presence of the thiol reactant.¹⁹ However, there is no reported study on the reactivity of BBA with thiol reactants.

Herein, we report the first use of Ae-based catalysts for the generation of BBA via the reduction of CO₂ (Scheme 1d). The in situ generated BBAs were then used as C₁ source to generate compounds featuring C-S bonds and notably new borylated hemithioacetal compounds under mild conditions.

Scheme 1. a) Alkaline earth-catalyzed CO₂ hydroboration into pinBOCH₃, b) BBA as methylene transferring agent toward C-N, C-O, C-P and C-C bond formation, c) proposed monoborylated hemiacetal, d) Selective Alkaline earth-catalyzed 4e-reduction of CO₂ and transformation of the produced BBA as an intermediate to generate S-CH₂ bonds.



RESULTS AND DISCUSSION

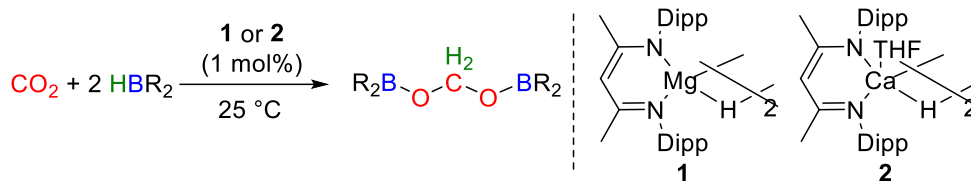
The B(C₆F₅)₃ adducts **A** and **B** (Scheme 1a) were shown to catalyze the CO₂ hydroboration with HBpin.⁴ We wanted to probe if in the absence of B(C₆F₅)₃, the related hydrido [Mg] (**1**) and [Ca] (**2**) complexes would be able to initiate CO₂ hydroboration. However, complexes **1** and **2** exhibited rather poor catalytic reactivity with HBpin since, after few days at 60 °C, complexes **1** and **2** led to only 20 and 36 % conversion of HBpin into a mixture of 2e-, 4e- and 6e- reduction products (ESI). We¹¹ and others^{10, 20-22} have shown that the nature of the hydroborane is important in CO₂ hydroboration in general and in the level of reduction of CO₂ in particular. We thus probed the reduction with 9-BBN and HBCy₂ (Table 1, Figure 1). The catalytic reactivity of complexes **1** and **2** was evaluated with 9-BBN since this reductant is the most encountered in CO₂ hydroboration to form BBA (Figure 1). Interestingly, a very selective transformation was observed for the 4e- reduction level of CO₂ at room temperature in a rather efficient manner. With 1 mol % catalytic loading, BBA^{BBN} was indeed obtained in 79 % and 87 % in situ yields for **1** and **2**, respectively, under 1 atm of CO₂ (Table 1). The complete reactions occurred in 7 h 25 and 1 h 40 for **1** and **2**, respectively, leading to TON of 79 and 87 and TOF of 11 and 52 h⁻¹. The conversion of 9-BBN was also monitored. The measured high conversion rates (above 94 %) were a good indicator that subsequent reactions involving the in situ generated

Table 1. Hydroboration of CO₂ to BBA^{BBN} and BBA^{Cy} catalyzed by complexes **1 and **2**.**

BBA can be envisioned since a limited amount of hydroborane remained. A small amount of formoxyborane (2e- reduction, R₂BOCHO) and methoxyborane (6e- reduction, R₂BOCH₃) were also detected (Table 1, Figure 1).

Recently, HBCy₂ was employed in CO₂ hydroboration reactions, selectively yielding the corresponding BBA^{Cy}.¹³ The iron hydride catalytic system, which was used at mild temperature of 25 °C, exhibited the highest reported TOF of 546 h⁻¹ for BBA generation, with a in situ yield of 91 % in 10 min of reaction. The use of this reductant, in the presence of 1 mol% of catalyst **1** or **2**, led selectively to BBA^{Cy} in high in situ yields of 95 and 90 %, in only 18 and 19 min, respectively (Table 1). The calculated TOF of 317 and 284 h⁻¹ measured with **1** and **2**, respectively, were particularly high for CO₂ hydroboration reaction catalyzed by Ae-based complexes (Scheme 1a) and also in BBA synthesis from CO₂.

The higher reactivity of 9-BBN compared to HBpin might come from the higher hydride donor ability calculated for 9-BBN vs HBpin.²³ This would implicate that the H-B addition onto the Ae-O bond is the rate determining step after CO₂ activation by the Ae-H moiety. One can assume that HBCy₂ exhibits its comparable hydride donor ability compared to 9-BBN.



HBR ₂	Cat	Time	In situ yield of BBA (%)	TON	TOF/h ⁻¹	In situ yield of R ₂ BOCHO (%)	In situ yield of R ₂ BOCH ₃ (%)	Remaining HBR ₂ (%)
9-BBN	1	7h25	79	79	11	3	12	6
	2	1h40	87	87	52	2	5	5
HBCy ₂	1	18 min	95	95	317	-	-	5
	2	19 min	90	90	284	9	-	2

Reaction conditions: 1 atm CO₂, 0.13 mmol HBR₂, 1 mol% catalyst, 650 μl THF-*d*₈, 25 °C. Yields were calculated in situ in reference to hexamethylbenzene as an internal standard. TON numbers were calculated from BBA in situ yields.

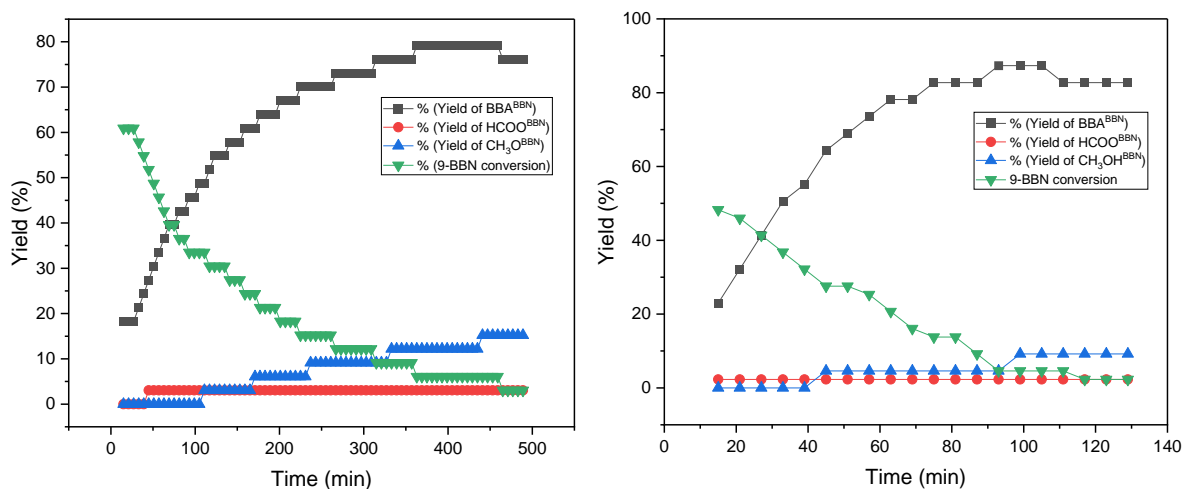


Figure 1. Plot of the evolution of reactant and products versus time in the hydroboration of CO₂ with 9-BBN mediated by 1 mol% of **1** (left) and **2** (right).

Having access to BBA compounds selectively from double CO₂ hydroboration, we explored their reactivity toward thiol compounds. We selected the [Ca] catalyst **2** to selectively generate BBA. We decided to investigate the reactivity of BBA^{BBN} rather than of BBA^{Cy}, because preliminary tests indicated a cleaner transformation (*vide infra*). ¹³CO₂ was employed as a powerful tool to closely follow the transformations at the carbon atom arising from CO₂ and of the methylene moiety (¹³CH₂) in the present case. The in situ generated ¹³C-BBA^{BBN} reacted at room temperature with thiophenol (Scheme 2). This reaction was followed by ¹H (Figure 2, S12, S13) and ¹³C{¹H} NMR (Figure S14). Within 16 h, the methylene signal of BBA^{BBN} at δ(¹H) 5.54 (d, ¹J_{CH} = 165.1 Hz) and δ(¹³C{¹H}) 87.0 was replaced by a close signal at δ(¹H) 5.38 (d, ¹J_{CH} = 159.5 Hz) and

δ(¹³C{¹H}) 70.6 in THF-*d*₈ in the presence of one or two equivalents of thiophenol (Scheme 2, Figure 2). This signal does not correspond to the expected dithioacetal compound **4** but was instead attributed to the borylated hemithioacetal **3**, generated with an in situ 57 % yield.²⁴ Compound **3** is a new compound fully characterized in situ by ¹H, ¹³C and ¹¹B NMR spectroscopy. The relative integration indicated the presence of only one phenyl group per methylene moiety and the scalar connection of the methylene with a boron nucleus was demonstrated with ¹H-¹¹B HMQC NMR analysis (Figure S5). The presence of one equivalent of borinic acid R₂BOH completed the stoichiometry of the transformation. While the presence of a second equivalent of thiophenol, or prolonged reaction time (16 h) at 80 °C, did not yield the dithioacetal compound **4**, the addition of sulfuric acid enabled such transformation. As shown in Figure 2,

upon the addition of sulfuric acid, the signals of compound **3** were readily replaced by resonances at $\delta(^1\text{H})$ 5.01 (d, $^1J_{\text{CH}} = 157.9$ Hz) and $\delta(^{13}\text{C}\{^1\text{H}\})$ 68.5 (s) that we tentatively attributed to the protonation of compound **3**. The protonation of the OBR₂

fragment enables the reaction with the second equivalent of thiophenol to generate compound **4** within 3 h at 80 °C, characterized by signals at $\delta(^1\text{H})$ 4.45 (d, $^1J_{\text{CH}} = 153.4$ Hz) and $\delta(^{13}\text{C}\{^1\text{H}\})$ 39.9 (s) with in situ 55 % yield.

Scheme 2. Reactivity of BBA^{BBN} toward thiophenol, 1,3-propanedithiol and 2-aminothiophenol.

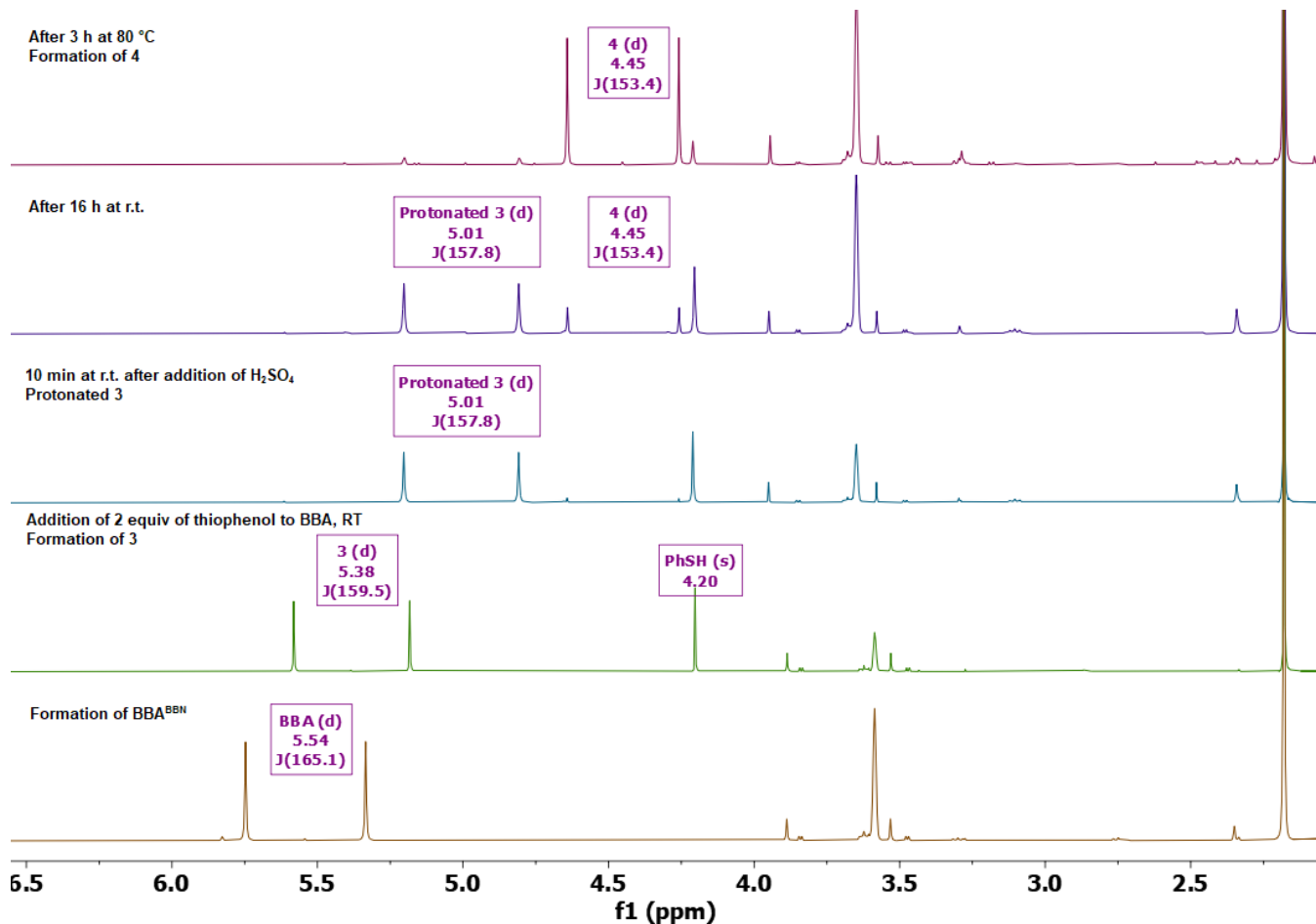
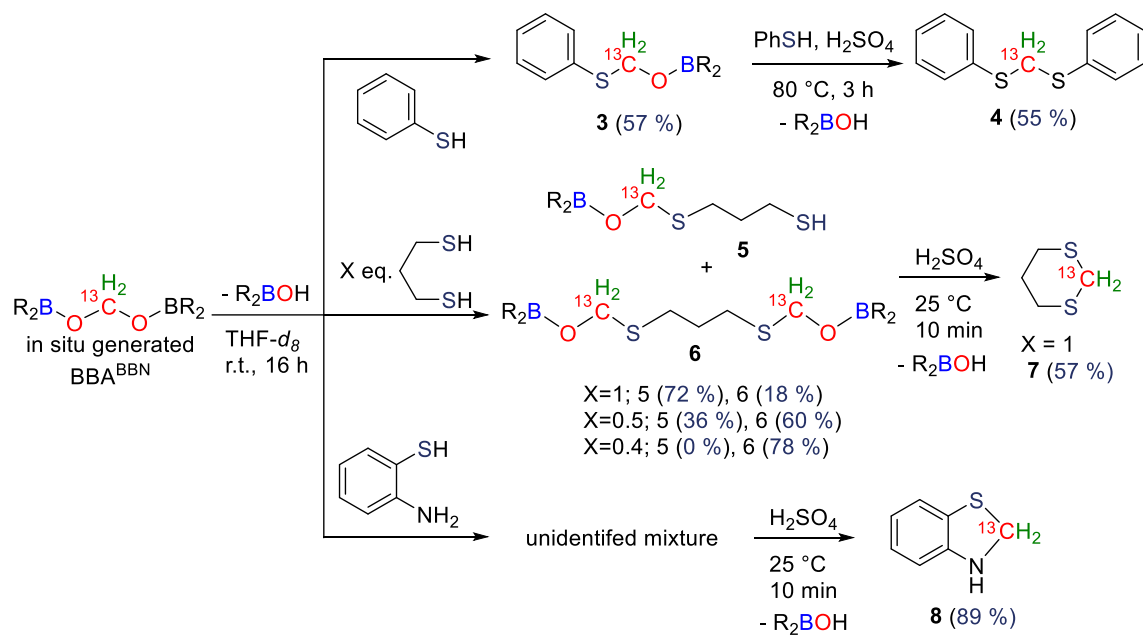
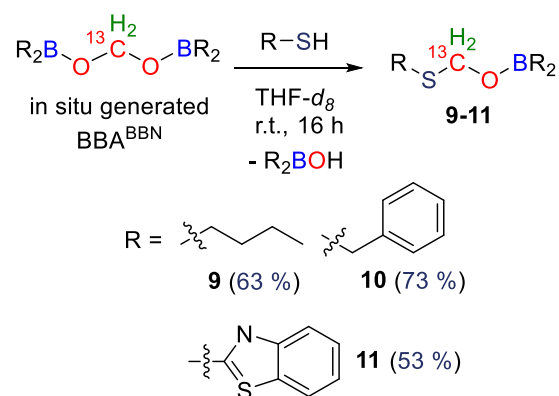


Figure 2. ^1H NMR spectroscopic monitoring of the transformation of BBA^{BBN} into **4** via **3**.

The reactivity of BBA^{BBN} toward thiols yielding hemithioacetals at room temperature under neutral conditions was also observed with a dithiol reactant. The reaction of BBA^{BBN} with one equivalent of 1,3-propanedithiol led to the generation of a major compound identified as the hemithioacetal compound **5** at 5.07 ppm and 68.7 ppm in ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR analyses, respectively, in 72 % in situ yield (Scheme 2). The connectivity with the borylated moiety (-OBBN) was confirmed by ^1H - ^{11}B HMQC NMR correlation (Figure S20). In addition, another compound was observed in smaller amount which features very similar NMR signatures. It corresponded to the diborylated hemithioacetal **6** generated in 18 % in situ yield. Longer reaction time (up to 3 days) and higher temperature up to 95 °C did not modify the amount of **5** and **6** in solution. However, the addition of sulfuric acid to the mixture led to the formation of the dithiane **7** in 57 % in situ yield in 10 min. The formation of the diborylated compound **6** was favored by adapting the stoichiometry: the addition of 0.4 equivalent of 1,3-propanedithiol to BBA^{BBN} resulted in the generation of compound **6** in 78 % in situ yield. The product **6** was also generated with similar stoichiometry from BBA^{Cy} , however, with a lower 60 % in situ yield based on BBA^{Cy} and with the presence of unidentified side products. When in situ generated BBA^{BBN} was reacted with 2-aminothiophenol, the complete conversion of the BBA was observed at room temperature within 16 h into an unidentified mixture (Figure S36, S37). Only the addition of sulfuric acid to the mixture generated 2,3-dihydrobenzothiazole compound **8** in 89 % in situ yield, based on BBA, within 10 min (Scheme 2).

Interested by the formation of hemithioacetal, the reactivity of BBA^{BBN} was further investigated with 1-butanethiol, benzyl mercaptan and 2-mercaptobenzothiazole (Scheme 3). In each case, the corresponding hemithioacetal product was obtained after 16 h at room temperature with in situ yields ranging from 53 to 73 %. The methylene fragments were characterized at $\delta(\text{CH}_2)$ 5.38, 5.06, 4.94 and 6.32 in the ^1H NMR spectra of **3** and **9-11**, respectively, whereas in the $^{13}\text{C}\{^1\text{H}\}$ spectra, the range is narrower ($67.1 < \delta(\text{CH}_2) < 70.9$).

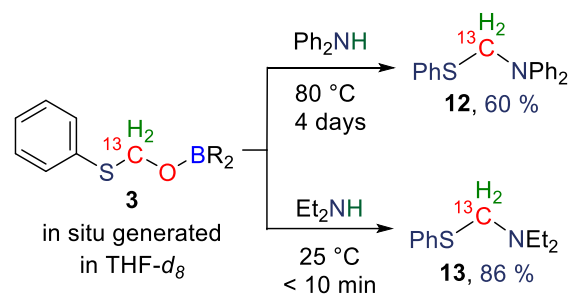
Scheme 3. Reactivity of BBA^{BBN} toward various thiol reactants.



Hemithioacetals are compounds usually obtained from the reaction of thiols with carbonyl derivatives. In many cases, this reaction is reversible, precluding their isolation,²⁵⁻²⁶ although some hemithioacetal could be isolated mostly when embedded in a cycle.²⁷⁻²⁸ In our case, the reaction with BBA enabled a novel access to hemithioacetals in general, while the presence

of the boryl moiety ensured the stability of this type of products. Moreover, the characterization of compounds **3**, **5**, **6**, and **9-11** showed that BBA derivatives react with only one equivalent of thiol, validating the possible formation of the analogous intermediate **K** (Scheme 1c). This finding also suggests a sequential mechanism and hence, we hypothesized that the presence of the sulfur atom deactivates the hemithioacetal with respect to a second nucleophilic attack of a second equivalent of thiol. We also showed that phenol did not react with compound **3**. Postulating that these reactants were not nucleophilic enough, we tested secondary amines. The addition of diphenylamine onto compound **3** led to the formation of the aminomethyl sulfide **12** in 60 % in situ yield after 4 days at 80 °C (Scheme 4). Interestingly, diethylamine afforded the related amino-methyl sulfide **13** in 86 % in situ yield in less than 10 min at 25 °C, further substantiating the importance of the nucleophilicity of the reactant. Amino-methyl sulfides were useful compounds for transferring the amino-methyl fragment.²⁹⁻³⁰

Scheme 4. Reaction of compound **3** toward secondary amine.



CONCLUSION

In conclusion, we have shown that earth-abundant complexes are able to catalyze CO_2 hydroboration to BBA. The [Ca]-based catalytic system exhibited very efficient catalytic properties, especially when associated with HBCy_2 . This result shows that Ae-based complexes may be employed for accessing a wider range of CO_2 reduction stage by modifying the nature of the applied hydroborane. The selective access to BBA was used to further probe the reactivity of the products from CO_2 hydroboration as intermediate in condensation reaction toward thiol. Surprisingly, the reaction does not lead to dithioacetal under mild neutral conditions but rather to stable hemithioacetal compounds **3**, **5**, **6**, **9-11**. This represents a new synthetic pathway to hemithioacetal and also shows that such kind of intermediates are likely in condensation reaction involving BBA. The activation of the hemithioacetal has been probed using acidic conditions leading to the expected dithioacetals and aminomethyl sulfide. With secondary amines that stronger nucleophiles, the condensation of the second OBR_2 fragment to generate aminomethyl sulfides is realized. Further work will aim at gaining insight into kinetic differences between the Mg- and Ca-based catalysts on the one hand and between the two hydroboranes on the other.

EXPERIMENTAL SECTION

General Information. All reactions with air and moisture sensitive compounds were carried out using standard Schlenk line and glovebox techniques under inert atmosphere of either nitrogen or argon. Solvents were dried either over KOH and subsequently distilled over sodium/benzophenone under nitrogen atmosphere or using an MBraun SPS column prior to use. Deuterated solvents were dried either over

sodium, degassed, and distilled under nitrogen atmosphere and stored under nitrogen with sodium or freeze-pump-thaw degassed and stored under argon over 4 Å molecular sieves. All substrates were purchased from Alfa Aesar, abcr, SigmaAldrich or TCI and used without further purification. The purity of the compounds was controlled by NMR spectroscopy. Quick Pressure Valve NMR tubes were used for the reactions with CO₂. NMR experiments were conducted in pressurizable NMR tubes. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker Avance III 400 (BBO, BBFO probes), Avance II HD 500 (BBO Prodigy probe), and Avance neo 500 (BBFO Prodigy probe) spectrometers. Chemical shifts are reported in parts per million, relative to SiMe₄ for ¹H and ¹³C analyses. Chemical shifts for ¹H and ¹³C analyses are relative to TMS and for ¹¹B analysis to F₃B.Et₂O. Mg-H complexes **1**³¹ and **2**³² were synthesized according to literature procedure. The in situ yields determined for products **3-13** are based on BBA against hexamethylbenzene as internal standard. Compounds **3-8**, **11-13** were analyzed by ¹H NMR with relaxation time of 30 s to ensure a proper integration and thus yield determination. The in situ yields of **9** and **10** were however determined from ¹H NMR analysis with relaxation time of only 1 s, leading to a slightly higher uncertainty of the resulting yields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. It includes experimental details, compounds synthesis and characterization.

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