

Hydroboration of Carbon Dioxide Using Ambiphilic Phosphine–Borane Catalysts: On the Role of the Formaldehyde Adduct

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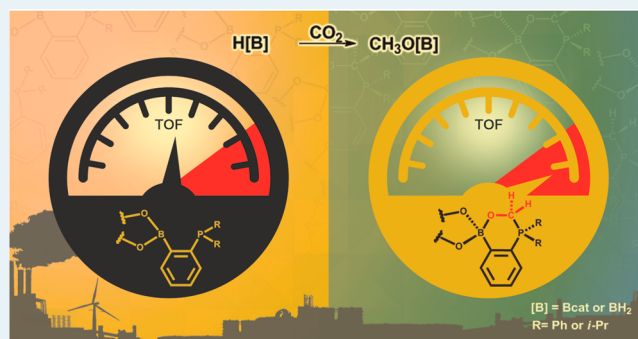
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Supporting Information

ABSTRACT: Ambiphilic phosphine–borane derivatives $1\text{-B(OR)}_2\text{-2-PR}'_2\text{-C}_6\text{H}_4$ ($\text{R}' = \text{Ph}$ (**1**), $i\text{Pr}$ (**2**); $(\text{OR})_2 = (\text{OMe})_2$ (**1a**, **2a**); catechol (**1b**, **2b**) pinacol (**1c**, **2c**), $-\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}-$ (**1d**)) were tested as catalysts for the hydroboration of CO_2 using HBcat or $\text{BH}_3\cdot\text{SMe}_2$ to generate methoxyboranes. It was shown that the most active species were the catechol derivatives **1b** and **2b**. In the presence of HBcat , without CO_2 , ambiphilic species **1a**, **1c**, and **1d** were shown to transform to **1b**, whereas **2a** and **2c** were shown to transform to **2b**. The formaldehyde adducts $\mathbf{1b}\cdot\text{CH}_2\text{O}$ and $\mathbf{2b}\cdot\text{CH}_2\text{O}$ are postulated to be the active catalysts in the reduction of CO_2 rather than being simple resting states. Isotope labeling experiments and density functional theory (DFT) studies show that once the formaldehyde adduct is generated, the CH_2O moiety remains on the ambiphilic system through catalysis. Species $\mathbf{2b}\cdot\text{CH}_2\text{O}$ was shown to exhibit turnover frequencies for the CO_2 reduction using $\text{BH}_3\cdot\text{SMe}_2$ up to 228 h^{-1} at ambient temperature and up to 873 h^{-1} at $70\text{ }^\circ\text{C}$, mirroring the catalytic activity of **1b**.

KEYWORDS: organocatalysis, carbon dioxide reduction, methanol, frustrated Lewis pairs, hydroboranes, ambiphilic systems



INTRODUCTION

The general consensus of the scientific community on the role of greenhouse gases on global climate changes has led to several initiatives to limit their emissions. As a consequence, a large number of contributions on the search for economical and efficient ways to sequester and valorize carbon dioxide, the principal gas which causes climate change, have appeared. Nowadays, several technologies are used in order to capture carbon dioxide from flue exhausts of major producers but sequestration remains a costly solution.¹ One way to make the capture of CO_2 more economically viable is in its valorization by using this molecule as a C-1 building block for the synthesis of valuable chemicals.² One transformation that has attracted much attention is the reduction of carbon dioxide to methanol, which is at the core of the methanol economy, as promoted by Nobel laureate George A. Olah.³ Several heterogeneous systems are known to catalytically reduce carbon dioxide to methanol, and some of these technologies are now commercialized.³ Nevertheless, the search for novel catalysts is still ongoing, notably using homogeneous systems which give

the promise for more active and selective processes. In that regard, some transition metal-based systems have been used for the reduction of carbon dioxide to formic acid,⁴ formate,⁵ formaldehyde,⁶ methanol,^{6d,7} methane,⁸ acetals,⁹ and carbon monoxide.¹⁰

In the past few years, there have been many important developments in the design of metal-free catalytic systems for the reduction of carbon dioxide. Indeed, some highly reactive species such as aluminum¹¹ and silylium cations¹² have been shown to reduce carbon dioxide with low selectivity to methane, methanol, and other alkylation side-products. FLP (frustrated Lewis pair) systems, even if they are known to bind carbon dioxide,¹³ have demonstrated very limited efficiency in its reduction.^{14,15} Since the seminal report by Ying and co-workers that *N*-heterocyclic carbenes can reduce carbon dioxide in the presence of hydrosilanes to methoxysilanes, which upon

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hydrolysis yield methanol,¹⁶ there have been few other organocatalytic systems reported for carbon dioxide reduction. Among these figures the report by Stephan that some phosphine–borane systems derived from 9-BBN catalyze the hydroboration of CO₂.¹⁷ For their part, Cantat and co-workers demonstrated that strong nitrogen bases, such as guanidines and amidines can be used as organocatalysts for the reduction of CO₂ to formamides using hydrosilanes^{18a} or to methoxyboranes using 9-borabicyclo[3.3.1]nonane (9-BBN) and, although with very low turnover frequency, HBcat (cat = catechol).^{18b} It was recently reported that bidentate Lewis bases, such as proton sponge, can also act as a catalyst for the reduction of carbon dioxide using BH₃·SMe₂ as a reductant^{18c,d} and that even NaBH₄ can catalyze the reduction of carbon dioxide using BH₃ adducts.^{18e} Moreover, Cantat and co-workers reported the methylation of amines with carbon dioxide and 9-BBN mediated by proazaphosphatranes super-bases.^{18f} However, these last systems, although active, exhibit either low turnover numbers or low turnover frequencies.

One of the most active metal-free systems for the reduction of carbon dioxide to date is 1-Bcat-2-PPh₂-C₆H₄ (**1b**), which can be generated in situ from the addition of HBcat to precatalyst Al(2-PPh₂-C₆H₄)₃.¹⁹ **1b** can generate methoxyboranes of general formula CH₃OBR₂ from several hydroboranes (HBR₂), such as catecholborane, pinacolborane, and BH₃·SMe₂, which in turn can be hydrolyzed to methanol.²⁰ Although such a process has limited commercial potential because of the cost of boranes, it serves as an excellent model to understand the mechanism of FLP-derivatives in the catalytic functionalization of unsaturated substrates such as carbon dioxide. Indeed, the very high turnover frequency (TOF), which can reach 973 h⁻¹, and the turnover numbers (TONs) obtained, which exceed 2950 at 70 °C, surpass that of the most active transition metal catalysts. An in-depth density functional theory (DFT) study of this system using HBcat as reductant allowed postulating that the activation of both the catecholborane and CO₂ in a concerted fashion led to much lower transition state energies than classical reduction pathways, a process that does not occur without catalyst.²¹ In order to optimize this class of catalyst, we were interested in looking at the influence of the substituents on the phosphine and borane parts. Herein, we report that the influence of the phosphine and the borane moieties on the catalyst is of limited importance because of substitutions that occur prior to the beginning of the catalytic activity. Notably, the formaldehyde generated forms an adduct with the phosphine–borane that turns out to be an active catalyst for the reduction of carbon dioxide rather than only a resting state as previously postulated. DFT calculations suggest that the dual activation of the borane and carbon dioxide plays a key role in the reduction process.

RESULTS AND DISCUSSION

Efficiency of 1-B(OR)₂-2-PR'₂-C₆H₄ Derivatives As Catalysts for the HBcat Hydroboration of CO₂. Phosphine–boranes of the general structure 1-BR₂-2-PR'₂-C₆H₄ have been reported before and used extensively as ligands for transition metals.²² Some of these metal-free species have shown a large range of activities, notably in the fixation, splitting, and transfer of singlet dioxygen,^{23a} in the bifunctional organo-catalyzed Michael addition^{23b} and in the trapping of reactive intermediates of organic transformations.^{23c,d} In order to better understand the importance of structural parameters of these phosphine–boranes derivatives on the catalytic activity,

the synthesis of 1-B(OR)₂-2-PR'₂-C₆H₄ derivatives with diphenyl- and di-*iso*-propyl-phosphine moieties (R' = Ph and *i*Pr) was envisioned (Figure 1).

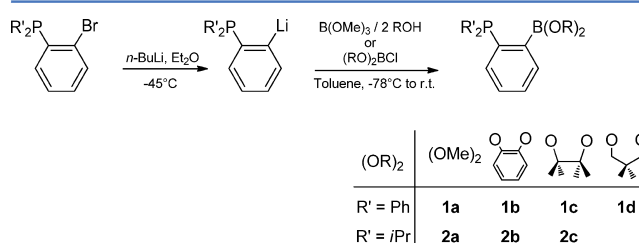


Figure 1. Synthesis of the various derivatives of general formula 1-B(OR)₂-2-R'₂P-C₆H₄ tested in the course of this study.

The 1-B(OR)₂-2-PPh₂-C₆H₄ derivatives (R₂ = catechol (**1b**), pinacol (**1c**), and -OCH₂C(CH₃)₂CH₂O- (**1d**)) were easily synthesized from the addition of the corresponding diols to in situ generated 1-B(OMe)₂-2-PPh₂-C₆H₄ (**1a**).^{23b} The isolation of the latter compound was also possible on the gram scale but proved to be quite sensitive to hydrolysis. On the other hand, the reaction of catechol with 1-B(OMe)₂-2-P(*i*Pr)₂-C₆H₄ (**2a**) surprisingly did not yield the expected 1-Bcat-2-P(*i*Pr)₂-C₆H₄ (**2b**), although the generation of the pinacol derivative 1-Bpin-2-P(*i*Pr)₂-C₆H₄ (**2c**) was successful using a similar reaction pathway. It was however possible to synthesize the desired analogue **2b** by the electrophilic trapping of 1-Li-2-P(*i*Pr)₂-C₆H₄ with ClBcat. Unfortunately, species **2b** proved to be particularly unstable in solution (Figure S18 in the Supporting Information (SI)), which might be caused by redistribution of the catechol moiety promoted by the nucleophilic phosphine,²⁴ and had to be protected by coordination to borane, generating species 1-Bcat-2-[P(*i*Pr)₂·BH₃]-C₆H₄ (**2b**·BH₃).

The catalytic activity of catalysts **1a–d**, **2a**, **2b**·BH₃, and **2c** toward the hydroboration of CO₂ was evaluated first using HBcat as a reducing agent under approximately 2 atm of CO₂ in C₆D₆.²⁵ As can be seen in Table 1 (entries 1–3, 6, and 9), species **1a–c**, **2a**, and **2c** exhibit similar catalytic activity for the formation of methoxyboranes, sustaining turnover frequencies between 46 to 56 h⁻¹ range in the first 105 min of reaction. A stoichiometric amount of catBOBcat was also formed during the process, as previously characterized for this system.^{20a} The exception is **2b**·BH₃, presumably because of the BH₃ protection of the phosphine moiety (entry 7). However, this problem is circumvented after some time since a TON of 74 was observed after 12 h of reaction (entry 8). Species **1d** is very slow to start (entry 4), showing insignificant production of methoxyboranes after 105 min of reaction, but with increasing activity as time goes, reaching TON of 48 after 4 h (entry 9).

Spectroscopic Monitoring of the Reduction Process.

In order to rationalize the similarities in catalytic activity of the different phosphine–boranes species and explain the difference of reactivity for the neopentyl glycol derivative **1d**, the CO₂ reduction using HBcat was monitored using ¹H and ³¹P{¹H} NMR spectroscopy. As previously reported, one species at -1.0 ppm was observed by ³¹P{¹H} NMR spectroscopy when **1b** was used as catalyst, which was attributed to the formaldehyde adduct 1-Bcat-2-PPh₂-C₆H₄·CH₂O (**1b**·CH₂O). Interestingly, it was observed that **1b**·CH₂O was also present at the end of the CO₂ reduction catalytic experiments when using any of the **1a–d** derivatives as catalyst. In order to account for possible

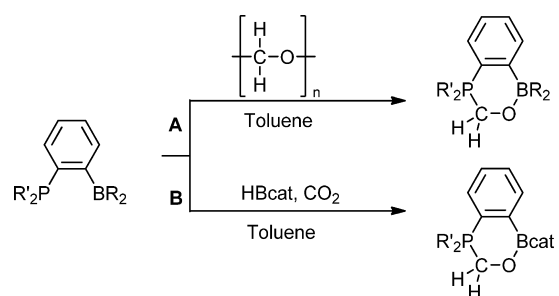
Table 1. Catalytic Hydroboration of 2 atm of CO₂ Using HBcat^a

$\text{CO}_2 + 3 \text{HBcat} \xrightarrow[70^\circ\text{C, C}_6\text{D}_6]{\text{PB catalyst}} \text{H}_3\text{C}-\text{OBCat} + \text{CatBOBCat}$					
entry	catalyst	borane	time (min)	TON ^b	TOF ^b (h ⁻¹)
1	1a	HBcat	105	92	53
2	1b	HBcat	98	98	56
3	1c	HBcat	105	81	46
4	1d	HBcat	105	1	<1
5	1d	HBcat	240	48	12
6	2a	HBcat	105	84	48
7	2b·BH ₃	HBcat	105	0	0
8	2b·BH ₃	HBcat	720	74	6
9	2c	HBcat	105	75	43

^aReaction conditions: In a J-Young NMR tube, 530 μmol of catecholborane (56.4 μL) was added to a mixture of 5.3 μmol of catalyst (~0.6 mL of stock solution at ~8.8 mmol/L) and an internal standard of hexamethylbenzene (2 mg, 3.3 g/L) in C₆D₆. The final concentration of catalyst is 8.1 mM. The J-young NMR tube was placed under ~2 atm of CO₂ and was heated at 70 °C. The catalysis was followed by ¹H NMR spectroscopy. ^bTurnover numbers (TONs) and turnover frequencies for the formation of CH₃OBCat according to the number of hydrogen atoms transferred to CO₂ based on NMR integration of the corresponding resonance with internal standard.

transformations of the catalyst during the reduction process, the reactions of species 1a–d with HBcat were carried out. It was found that 1a, c, and d readily convert to species 1b when 5 equiv of catecholborane was added to these species in the absence of CO₂. However, species 1d was shown to undergo such replacement more slowly than the other ambiphilic species. Monitoring the catalytic reduction of CO₂ with 1d as a catalyst showed that catalysis did not begin until it transforms to 1b. Similarly, the CO₂ reduction reactions using 2a, 2b·BH₃, or 2c as catalysts allowed the observation of a single phosphorus containing species by ³¹P{¹H} NMR at δ = 14.8 as the resting state of the reaction. The addition of HBcat to 2b·CH₂O (vide infra) in solution without the presence of CO₂ gave the same resonance observed under catalytic conditions at ~14 ppm, suggesting that the latter species consist in a Lewis adduct between 2b·CH₂O and HBcat, presumably by an interaction between the HBcat and one O adjacent to B, although the exact mode of interaction could not be determined experimentally. This transformation implies the reduction of CO₂ to formaldehyde, as previously reported for the PPh₂ derivatives, but also the substitution of the pinacol moiety on boron by a catechol moiety. Similarly to the case of the –PPh₂ catalysts, the formaldehyde adduct 2b·CH₂O is the resting state of the CO₂ reduction reaction.

Synthesis of the Formaldehyde Adducts and Labeling Experiments. As observed in Scheme 1, the formaldehyde adduct of 1b can be prepared and isolated by heating the phosphine–boranes 1b in the presence of excess paraformaldehyde. Unfortunately, other phosphine–boranes formaldehyde adducts based on the PPh₃ framework could not be isolated. In fact, 1a decomposed when heated with paraformaldehyde. While 1c is stable in the presence of paraformaldehyde, its binding of formaldehyde was found to be reversible and the adduct 1c·CH₂O could not be isolated in the solid form. Consequently, 1c·CH₂O could be prepared in situ and characterized by NMR spectroscopy, but its catalytic activity could not be quantified. In CDCl₃, the methylene resonances

Scheme 1. Synthesis of Formaldehyde Adducts of Phosphine Boranes^a

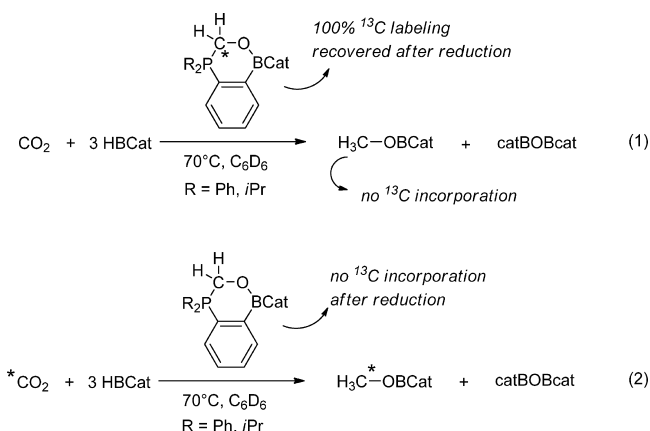
^a1b·CH₂O: path A using 1b, 80 °C, 16 h. 1b-¹³CH₂O: path B using 1b, ¹³CO₂, 5 HBcat, 80 °C, 16 h. 1c·CH₂O: path A, using 1c, 70 °C, 15 min. 2b·CH₂O: path B using 2c, 3 HBcat, 80 °C, 12 h. 2c·CH₂O: path A, using 2c, 70 °C, 15 min.

were observed by ¹H NMR spectroscopy at 5.37 ppm for both 1b·CH₂O and 1c·CH₂O, which is consistent with the change in hybridization of the carbon atom and with the loss of planarity of the aldehyde. In the ³¹P{¹H} NMR spectra, 1c·CH₂O was characterized by a singlet at –5.5 ppm, while 1b·CH₂O resonates at δ = –3.5. The ¹¹B NMR spectra show signals consistent with tetravalent boron atoms at 5.7 and 8.8 ppm for 1c·CH₂O and 1b·CH₂O, respectively. The formaldehyde adducts of the PiPr₂ derivatives appeared to be more stable than their PPh₂ counterparts. Species 2b·CH₂O was isolated in quantitative yield by the addition of 3 equiv of HBcat to 2c under 1 atm of CO₂ in C₆D₆ or by the addition of 30 equiv of HBcat to species 2c·CH₂O (Scheme 1). This species has a ³¹P NMR chemical shift of δ = 12.2 and the CH₂ resonance was observed at δ = 4.96 in the ¹H NMR spectrum. 2c·CH₂O was isolated by the addition of paraformaldehyde to species 2c in toluene at 70 °C and was characterized by ³¹P NMR (δ = 7.7).

In order to verify if the aldehyde adduct is only a resting state or a significant part of the active catalyst, labeled 1b-¹³CH₂O and 2b-¹³CH₂O were prepared directly from ¹³CO₂. 1b-¹³CH₂O was synthesized by exposing 1b to ca. 2 atm of ¹³CO₂ in a closed Schlenk vessel in the presence of 5 equiv of catecholborane. The resulting white precipitate was isolated and washed several times with toluene to yield pure 1b-¹³CH₂O. The ³¹P{¹H} NMR spectrum for 1b-¹³CH₂O shows a characteristic doublet at –3.5 ppm with a ¹J_{C–P} of 57 Hz. In the ¹H NMR spectrum, the CH₂O resonance was found as a doublet at 5.37 ppm with a ¹J_{C–H} of 151 Hz. Interestingly, when this species was used as catalyst for the hydroboration of CO₂ using HBcat (Scheme 2, eq 1), no ¹³C incorporation was observed in the methoxyborane formed and the ¹³C–³¹P coupling within the formaldehyde adduct could be observed by NMR spectroscopy throughout the catalytic process. Consistently, when 1b·CH₂O and 2b·CH₂O were used to reduce ¹³CO₂, no ¹³C incorporation was observed in the formaldehyde adducts. These experiments demonstrate that the CH₂O fragment bridging P and B is not reduced but stays coordinated on the ambiphilic molecule. Thus, the formaldehyde adduct is more than a resting state and is in fact the active species responsible for the fast reduction of CO₂ in the presence of ambiphilic phosphine–boranes 1 and 2.

DFT Studies of CO₂ Reduction Using Formaldehyde Adducts. In order to determine whether formaldehyde adduct 1b·CH₂O and 2b·CH₂O in the catalytic transformation, the possible interactions between HBcat and these species were

Scheme 2. Labeling Experiments Carried out with the Phosphine–Boranes Formaldehyde Adducts $1b \cdot CH_2O$ and $2b \cdot CH_2O$



studied using computational chemistry. In order to compare the energies with our previous computational studies, calculations were performed at the same level of theory (B97D/6-31G***) with the solvation effects (benzene) accounted for by the SMD model. As shown in Figure 2, several possible adducts could be optimized where the borane interacts with one of the oxygen on the phosphine–boranes species, notably from the catechol and the aldehyde moieties. Although the previously reported formaldehyde adduct remains the most thermodynamically stable adduct, many other minima could be located on the energy surface. Unsurprisingly, all the isomers have very similar energy values, making difficult the identification of one ground-state structure, especially when keeping in account the uncertainty of the method ($\pm 5 \text{ kcal}\cdot\text{mol}^{-1}$), and the possible involvement of fluxional processes and conformational changes.

Intrigued by the important number of isomers identified and by the possibility for the aldehyde adduct to be an active catalyst rather than a resting state, pathways for CO_2 reduction were investigated with $1b \cdot CH_2O$ acting as a catalyst. In the study of the reduction of CO_2 by $1b$, the lowest energy barriers were found upon simultaneous activation of the catecholborane by the Lewis base and of carbon dioxide by the Lewis acid. Direct reduction of carbon dioxide, once bound in a classical fashion by the phosphine and the borane of the catalyst, was found to require a much higher barrier (Scheme 3).²¹

After a thorough investigation of the possibilities for $1b \cdot CH_2O$ to act as a catalyst for CO_2 reduction, it was possible to

find three new transition states which all involve simultaneous activation of HBCat and CO_2 . In the first transition state, **TS1a** (-1.1 (28.6)), the $H(2)-O(1)$ distance of 2.15 Å suggests that the Lewis acidic activation is achieved through hydrogen bonding with one of the hydrogen atoms of the bound-formaldehyde (Figure 3). Although unusual, the activation of CO_2 by hydrogen bonding was suggested before in the Ni(II)(cyclam) electrochemical reduction of CO_2 to CO by Sauvage and co-workers²⁶ and in the reduction of CO_2 to sodium formate by an Ir(III) pincer complex by Hazari and co-workers.²⁷ Another interesting aspect of this transition state is the difference in B–O bond lengths. While the B(1)–O(4) bond of 1.38 Å is in the expected range, the B(1)–O(3) bond of 2.27 Å is significantly elongated, showing that the catechol group is disconnected and that the B-catechol ring is opened. The second transition state also involved the formation of an oxygenate species with HBCat, but this time from the opening of the formaldehyde adduct (**IM3**) (**TS1b**; 1.9 (29.6) $\text{kcal}\cdot\text{mol}^{-1}$). The oxygen atom of CO_2 is perfectly aligned with the Lewis acidic boron center. The B–O bond distance of 2.44 Å and the planar geometry around the boron center (sum of angles = 358.7°) suggest weak interaction with the carbon dioxide molecule. The third transition state with similar energy values than the two other transition states was also located starting from intermediate **IM5**, (**TS1c** -1.8 (26.3) $\text{kcal}\cdot\text{mol}^{-1}$). It was found to occur by a simultaneous delivery of a boronium/hydridoborate ion pair which would be formed from the transfer of the hydride from one B-catechol moiety to the other. In all these intermediates, the formaldehyde adduct plays an important role, either by activating the borane or the carbon dioxide. Once the hydride and the Bcat moieties are transferred to generate the catBOC(O)H species, the B–O bond that was broken in the transition state (from the Bcat in pathway A and from B–OCH₂ in pathways B and C) is regenerated to reform species $1b \cdot CH_2O$.

Comparing these transition states with the direct reduction of formaldehyde (**TS 1d**, 22.3 (38.8 $\text{kcal}\cdot\text{mol}^{-1}$)) supports the experimental observation that formaldehyde remains bound to the ambiphilic framework during catalysis. The transition states **TS1a–TS1c** were found to have free energies that are respectively 9.7, 8.7, and 12.0 $\text{kcal}\cdot\text{mol}^{-1}$ lower than the activation by the phosphine that was originally reported. Although it is likely that the initial formation of the aldehyde occurs through the phosphine–borane mechanism, the results reported herein show that the oxygen atoms are more potent than phosphorus in the activation of hydroboranes.

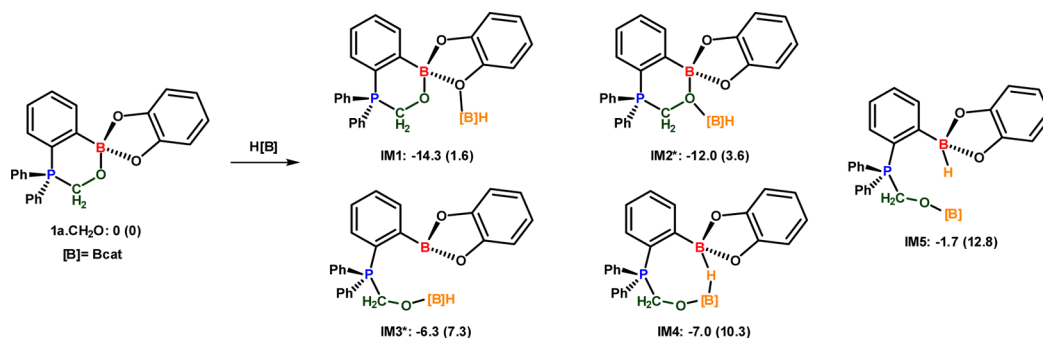
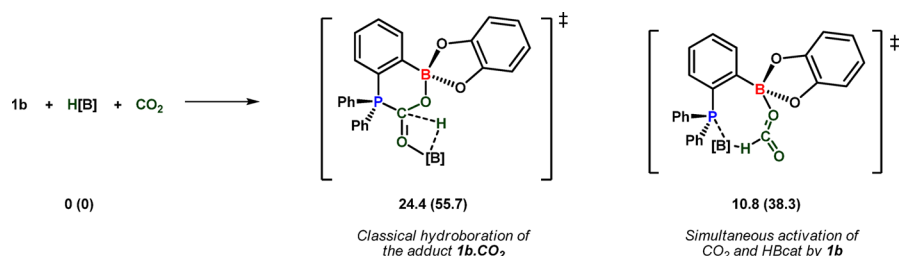
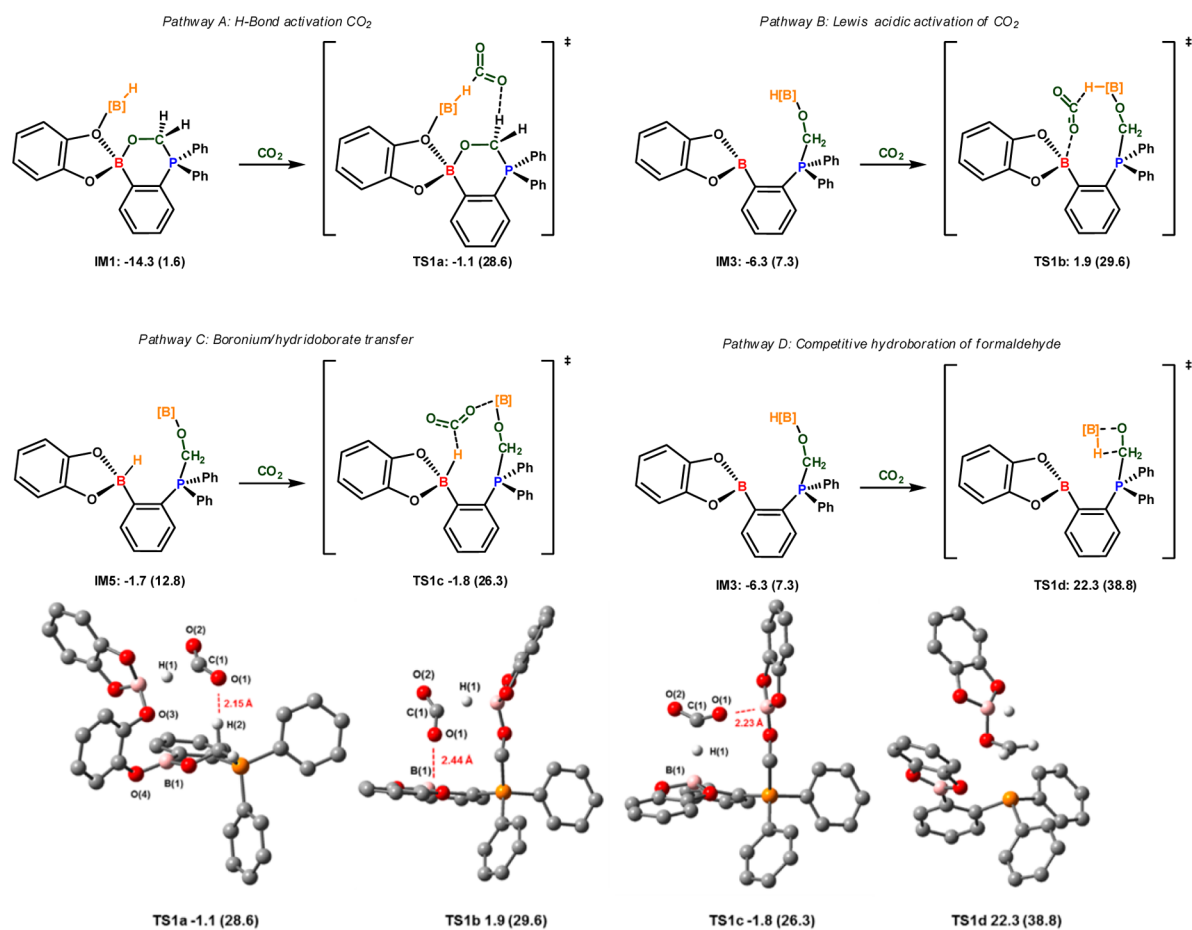


Figure 2. Some of the calculated adducts between the boranes ([B]H = HBCat) and species $1b \cdot CH_2O$ with calculated free enthalpy and free energy ($\text{kcal}\cdot\text{mol}^{-1}$) computed at B97D/6-31G***) with the experimental solvent (benzene) accounted for the SMD model. The * indicates that two minima were observed for two rotamers (see the [SI](#)).

Scheme 3. Previously reported transition states (and Energies in Kilocalories Per Mole) for the Hydroboration of CO₂ by **1b**^a^aH[B] = catecholborane.²¹Figure 3. Transition state structures for the hydroboration of CO₂ by **1b**·CH₂O and HBcat. Calculated free enthalpy and free energy (kcal·mol⁻¹) computed at B97D/6-31G** with the experimental solvent (benzene) accounted for the SMD model.

Catalytic Efficiency of Aldehyde Adducts in the Reduction of CO₂ using BH₃·SMe₂. The efficiency of the aldehyde adducts was then evaluated in the reduction of CO₂ using the dimethylsulfide–borane adduct as a reducing agent. BH₃·SMe₂ is a reagent of choice for the hydroboration of CO₂ since it is less reactive and dangerous than the diborane reagent B₂H₆ while possessing high hydrogen content by having three transferable hydrides per boron atom. Interestingly, no transition metal system has been reported to use BH₃ adducts for the reduction of carbon dioxide and only a limited number of organocatalysts can do such reaction, including **1b** that proved the most active to date, with TOF of 973 h⁻¹ at 70 °C.²⁰ To follow up on known literature, the values of TON and TOF were calculated according to the number of hydrogen atoms transferred on CO₂.

The catalytic reduction of CO₂ was carried out using **1a**–**1d** as catalysts (Table 2, entries 1–4). In these experiments, about 2 atm of CO₂ was added to a 8 mM solution of the catalyst in C₆D₆ containing 100 equiv of BH₃·SMe₂ in a J-Young NMR tube. As can be observed, both species **1a** and **1b** showed good activities, reaching TOF of 257 and 242 h⁻¹ in the first hour of reaction (Table 2, entries 1 and 2, respectively). There is a significant decrease in activity when the pinacol derivative was used, since only a TOF of 43 h⁻¹ was observed (Table 2, entry 3), whereas catalyst **1d** did not show significant activity (Table 2, entry 4). While the reduction of CO₂ using BH₃·SMe₂ and **1b** as catalyst proceeds rapidly at 70 °C, it was shown to be much slower at room temperature. As it was reported, the spectroscopic monitoring of the latter reaction reveals that it suffers from a long induction period before reaching its peak

Table 2. Catalytic Hydroboration of 2 atm of CO₂ Using BH₃·SMe₂^a

		PB catalyst			
		C ₆ D ₆		[B(OMe) _n O] _n + SMe ₂	
entry	catalyst	time (min)	T (°C)	TON ^b	TOF ^b (h ⁻¹)
1	1a	60	70	257	257
2 ^{20a}	1b	67	70	271	242
3	1c	60	70	43	43
4	1d	60	70	<1	<1
5	1b ·CH ₂ O	35	25	84	144
6	2b ·CH ₂ O	30	20	114	228
7	2b ·CH ₂ O	90	20	204	136
8	2b ·CH ₂ O	30	70	297	594
9 ^c	2b ·CH ₂ O	30	70	435	873
10 ^c	2b ·CH ₂ O	90	70	1005	670

^aReaction conditions: In a J-Young NMR tube, 530 μmol of BH₃·SMe₂ (56.4 μL) was added to a mixture of 5.3 μmol of catalyst (~0.6 mL of stock solution at ~8.8 mmol/L) and an internal standard of hexamethylbenzene (2 mg, 3.3 g/L) in C₆D₆ for entries 1–5, but in CDCl₃ for entries 6–10. The final concentration of catalyst is ~8.1 mM. The J-young NMR tube was placed under 2 atm of CO₂ and was heated at 70 °C. The catalysis was followed by ¹H NMR spectroscopy. ^bTurnover numbers (TONs) and turnover frequencies for the formation of [B(OMe)_nO]_n according to the number of hydrogen atoms transferred to CO₂ based on NMR integration of the corresponding resonance with internal standard. ^cThe reaction was performed under the same conditions but with a catalyst concentration of ~1.8 mM.

turnover frequency. The intermediates of the reaction were monitored using ¹H and ³¹P NMR spectroscopy. As long as species **1b**·BH₃ is the only one in solution, no significant reduction process is taking place. However, as soon as the presence of the formaldehyde adduct was observed, the catalytic reduction rate was shown to increase significantly, confirming that **1b**·CH₂O is playing a significant role on the catalytic reduction.

When carrying out the reduction of CO₂ in benzene at room temperature with **1b**·CH₂O as the catalyst, the rapid reduction of CO₂ was observed in the first minutes of reaction. In fact, within the 5 min needed for the acquisition of the first NMR spectrum, it was possible to ascertain a nominal TON value of 26 for the conversion of CO₂ to [MeOBO]_n, which can be associated with an initial TOF of >520 h⁻¹ (Figure 4). This reaction rate is significantly superior to previously observed catalytic activities at ambient temperature when using **1b** as the starting catalyst, especially when considering that a significant amount of the catalyst was not dissolved at this time. After 35 min, a TON of 84 was observed, corresponding to a TOF of 144 h⁻¹ (Table 2, entry 5).

The formaldehyde adduct **2b**·CH₂O was also evaluated with BH₃·SMe₂ as a reductant. The catalytic tests were performed in CDCl₃ to ensure good solubility. Accordingly, it was found that a 1 mol % of species **2b**·CH₂O could give over 99% of the conversion expected within 30 min, giving TON of 114 and TOF over 228 h⁻¹ at ambient temperature, which is slightly higher than the activity of **1b**·CH₂O (Table 2, entry 6). Letting the reaction run for 90 min increased the TON value to 204, while reducing the TOF to 136 h⁻¹ (Table 2, entry 7). Looking at the reactivity at 70 °C it was possible to observe that catalyst **2b**·CH₂O converted almost quantitatively BH₃·SMe₂ to methoxyboranes in 30 min, giving TON and TOF of 297 and 594 h⁻¹ (Table 2, entry 8), respectively, which under NMR

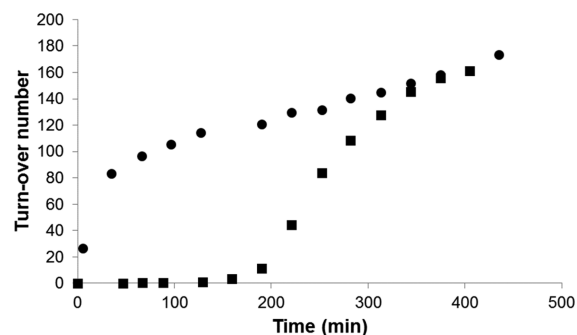


Figure 4. Number of turnovers for the reduction of CO₂ in [B(OMe)_nO]_n in the presence of 100 equiv of BH₃·SMe₂ as a reductant using 9 mM solution of (●) **1b**·CH₂O and (■) **1b** in C₆D₆. The reaction was carried out at room temperature using about 1–2 atm of CO₂ in a J-Young NMR tube. The exact pressure could not be measured, but under the loading present it is expected that CO₂ will be the limiting reagent since 1.5 atm is needed to obtain 100% yield (300 TON), explaining the lower rate at high conversion.

tube conditions surpass the catalytic activity of catalyst **1b**. Decreasing catalyst loading to 1.8 mM but keeping all the other parameters identical, it was possible to observe that catalyst **2b**·CH₂O could give a TON of 435 in the first 30 min (TOF of 873 h⁻¹), while running the reaction for 150 min increased the TON to 1005 (Table 2, entries 9 and 10). These results are of significant interest since some of the formaldehyde adducts exhibit higher stability than their phosphine–borane precursors, notably in the case of **2b**. Also, the high activity at ambient temperature and the absence of induction period contrasts drastically with all systems reported to date to reduce CO₂ using BH₃ derivatives which usually need induction periods and higher temperatures to proceed efficiently.

It should be noted that the increase in activity of the formaldehyde adducts compared to the ambiphilic phosphine–boranes is really counterintuitive, especially when comparing with the usual chemistry of Frustrated Lewis Pairs. Indeed, in latter systems, the activation of substrates such as molecular hydrogen and carbon dioxide is possible by preventing the formation of Lewis adducts between the two components of the FLP. Although such process is particularly important in hydrogen activation, it does not seem to play a similar role in the catalytic reduction of carbon dioxide. Indeed, the most important factor seems to be the activation of the reducing agent, which is done in the current system by interaction of the hydroborane with O atoms of the formaldehyde adduct; something that can be related to the activity of several borates in the reduction of carbon dioxide, including notably the BH₄⁻ salts that are well-known to reduce CO₂ in a stoichiometric fashion. It seems however that the simultaneous activation of the carbon dioxide by either hydrogen bonding or by a weak Lewis acid such as the boroncatecholate moiety is helping to lower significantly the transition state energy. As it was stated before, such weak Lewis acid can also prevent the formation of very stable formate adducts which might make difficult the release of the reduced species and high catalytic turnovers. The formaldehyde adducts **1b**·CH₂O and **2b**·CH₂O presented in this system have also the advantage to be quite stable to both air and water, which are significant advantages compared to some ambiphilic species, notably **2b**.

CONCLUSION

Ambiphilic species reported in this study all show the ability to hydroborate catalytically CO₂ to CH₃OBR₂ derivatives using catecholborane and BH₃·SMe₂. However, in the presence of catecholborane, all species undergo transformations to generate respectively **1b**·CH₂O or **2b**·CH₂O, which are believed to be the active catalysts in the latter reaction. Although the exact mechanism for such transformation is unknown, derivatives of **1b** and **2b** seem to be the favored species in such system. The latter reaction also puts in evidence the importance of possible redistribution occurring in such systems with the B–O bonds being quite kinetically labile. As it was demonstrated by using **1b**·¹³CH₂O and **2b**·¹³CH₂O as catalysts, the interaction between the formaldehyde and the phosphine–borane moiety seems to remain intact throughout catalysis. DFT modeling of possible transition states show that the ambiphilic activation remains possible, as it was proposed for species **1b**, but this time one oxygen atom, either from the formaldehyde or the catechol moieties, acts as Lewis base to activate the reducing agent, whereas the CO₂ is activated either by one borane or by hydrogen bonding with one hydrogen of the formaldehyde adduct. Species **2b**·CH₂O was shown to be the best catalyst at room temperature reported for this system, obtaining TOF of 228 h⁻¹. Although it represents a much harder challenge, we are currently interested in using such concept for the hydrogenation of carbon dioxide.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00189.

Detailed experimental procedures and additional DFT information (other calculated reaction pathways, Cartesian coordinates, free enthalpies, and energies) (PDF)

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Notes

The authors declare no competing financial interest.

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