Organocatalysis

Metal-Free Reduction of CO₂ with Hydroboranes: Two Efficient Pathways at Play for the Reduction of CO₂ to Methanol

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Abstract: Guanidines and amidines prove to be highly efficient metal-free catalysts for the reduction of CO₂ to methanol with hydroboranes such as 9-borabicyclo[3.3.1]nonane (9-BBN) and catecholborane (catBH). Nitrogen bases, such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (Me-TBD), and 1,8-diazabicycloundec-7-ene (DBU), are active catalysts for this transformation and Me-TBD can catalyze the reduction of CO₂ to methoxyborane at room temperature with TONs and TOFs of up to 648 and 33 h⁻¹ (25 °C), respectively. Formate HCOOBR₂ and acetal H₂C(OBR₂)₂ derivatives have been identified as reaction intermediates in the reduction of CO₂ with R₂BH, and the first C–H-bond formation is rate determining.

Experimental and computational investigations show that TBD and Me-TBD follow distinct mechanisms. The N–H bond of TBD is reactive toward dehydrocoupling with 9-BBN and affords a novel frustrated Lewis pair (FLP) that can activate a CO_2 molecule and form the stable adduct **2**, which is the catalytically active species and can facilitate the hydride transfer from the boron to the carbon atoms. In contrast, Me-TBD promotes the reduction of CO_2 through the activation of the hydroborane reagent. Detailed DFT calculations have shown that the computed energy barriers for the two mechanisms are consistent with the experimental findings and account for the reactivity of the different boron reductants.

Introduction

Carbon dioxide is an attractive C₁ building block for the production of chemicals and fuels because it is an economical, renewable, and nontoxic carbon source.^[1] Nonetheless, the kinetic and thermodynamic stability of CO₂ strongly limits the scope of molecules available from CO₂ and efficient catalysts are needed to promote its reduction. Hydrogen, hydrosilanes, and hydroboranes possess redox potentials that are well suited for the reduction of CO₂ to formic acid or methanol and recent efforts have led to the successful design of metal catalysts able to accelerate these reactions, most of them being based on noble metals. $^{\mbox{\tiny [2-10]}}$ Nonetheless, in the long term, sustainable technologies for the reduction of CO₂ must take into account the availability of such metal ions and the cost and/or toxicity. These limitations have urged the development of metal-free catalysts for the reduction of CO₂ and, so far, the hydrosilylation of CO₂ (to formic acid derivatives or methoxysilanes) has focused most research efforts, which have led to the successful development of organic catalysts.[3,4]

The reduction of CO₂ with hydroboranes (i.e., 9-borabicyclo-[3.3.1]nonane (9-BBN), pinacolborane (pinBH), and catecholborane (catBH)) was recently discovered by Guan and co-workers,

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who used nickel(II) complexes supported by phosphane pincer ligands I (Scheme 1).^[6] Based on mechanistic investigations, the authors proposed a catalytic mechanism that involved successive σ -bond metathesis reactions and the insertion of CO₂ into a reactive Ni–H bond. Consecutively, Bontemps and Sabo-Etienne described ruthenium–polyhydride complexes II able to promote the same catalytic transformation.^[7] Importantly, it was shown that the ruthenium system leads to the formation of an unexpected C₂ intermediate that results from the C–O



Scheme 1. Reported catalysts for the reduction of CO_2 to methanol with hydroboranes. The catalytic performances for **II** and **IV** are estimated from the results described in ref. [7, 9].



coupling of two CO₂ molecules. In 2012, Sgro and Stephan reported a ruthenium-tris(aminophosphine) complex III that exhibits a reactivity reminiscent of frustrated-Lewis-pair (FLP) systems and catalyzes the hydroboration of CO₂, with a modest activity.^[8] This collection of catalysts was recently enlarged by the contribution from Shintani and Nozaki (i.e., complex IV);^[9] however, the complexes developed by Guan and co-workers remain the most efficient catalysts so far in this reaction (Scheme 1). More recently, Fontaine and co-workers reported the first organic catalysts to promote the hydroboration of CO₂ by means of the ambiphilic phosphine-borane system $V_r^{[10a]}$ which exhibits a catalytic activity competitive with the metal systems I-IV, with a turnover number (TON) of 2950 and a turnover frequency (TOF) of 973 h^{-1} for the reduction of CO₂ with BH₃·SMe₂ as the reductant at 70 °C. Notably, under the conditions developed by Guan and co-workers (i.e., with catBH at RT), the TON and TOF of **V** drop to 34 and 17 h^{-1} , respectively. An alane version of ${\bf V}$ was developed recently by Fontaine and co-workers, which promotes the hydroboration of CO₂, albeit with lower catalytic activity and decreased stability.^[10b]

In 2012, our group demonstrated that guanidines and amidines were efficient metal-free catalysts for the reduction of CO_2 to formamide derivatives with hydrosilanes as reductants.^[4] Nitrogen bases, therefore, appear as promising candidates in the organocatalytic hydroboration of CO_2 , which is supported by recent findings that CO_2 can be reduced to the methanol level by using a stoichiometric amount of an amineborane moiety.^[11] Herein, we describe the successful utilization of commercially available nitrogen bases as organocatalysts for the hydroboration of CO_2 to methanol. Two distinct reaction pathways have been unveiled in this 6-electron reduction process, based on the isolation of reactive catalytic intermediates and DFT calculations, that depend on the nature of the catalyst.

Results and Discussion

A mixture of 9-BBN and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in a 40:1 ratio (i.e., 2.5 mol% catalyst loading) rapidly evolved under an atmosphere of CO₂ to produce the methoxyborane derivative CH₃OBBN with a TON of 26 after 27 hours at room temperature (Table 1, entry 2). A control experiment confirmed that a catalyst is needed to promote this transformation (Table 1, entry 1). This reaction is the second example of CO₂ hydroboration with a metal-free catalyst,^[10a] thus illustrating the potential of nitrogen bases in the catalytic reduction of CO₂. Under similar reaction conditions, a variety of nitrogen bases were tested as catalysts. Although 4-dimethylaminopyridine (DMAP), 1,4-diazabicyclo[2.2.2]octane (DABCO), and 1,8bis(dimethylamino)naphthalene (PS, Proton-sponge®) showed negligible catalytic activity, the guanidine and amidine moieties Me-TBD and DBU, respectively, proved to be highly efficient and led to complete reduction of CO₂ to the methoxy level within 7 hours at room temperature (Table 1, entries 3-7). Importantly, high TONs of 537, 648, and 351 can be achieved within 33 hours with TBD, Me-TBD, and DBU, respectively (Table 1, entries 11-13), which correspond to TOFs of 3.6-

Entry	Catalyst [(mol %)]	Borane (R ₂ BH)	T [°C]	t ^[a] [h]	TON ^[b]	TOF [h ⁻¹] ^[c]
1		9-RBN	25	> 48	no conve	rsion
2	TBD (2.5)	9-BBN	25	27	26	0.9
3	Me-TBD (2.5)	9-BBN	25	7	24	3.3
4	DBU (2.5)	9-BBN	25	, 7	22	3.2
5	DMAP (2.5)	9-BBN	25	48	11	0.2
6	PS (2.5)	9-BBN	25	>48	0	0
7	DABCO (2.5)	9-BBN	25	>48	0	0
8	TBD (1.0)	9-BBN	25	23	66	2.9
9	Me-TBD (1.0)	9-BBN	25	33	57	1.7
10	DBU (1.0)	9-BBN	25	17	63	3.6
11	TBD (0.1)	9-BBN	25	147	537	3.6
12	Me-TBD (0.1)	9-BBN	25	20	648	33
13	DBU (0.1)	9-BBN	25	50	351	6.9
14	Me-TBD (1.0)	catBH	25	168	54	0.3
15	DBU (1.0)	catBH	25	>200	0	0
16	DBU (1.0)	catBH	70	>200	0	0
17	TBD (1.0)	catBH	25	>200	0	0
18	TBD (1.0)	catBH	70	>200	0	0
19	2 (2.5)	9-BBN	25	27	26	0.9
20	4 (2.5)	9-BBN	25	217	23	0.1
21	4 (2.5)	9-BBN	70	180	20	0.1
22	5 (2.5)	9-BBN	25	84	24	0.3
23	5 (2.5)	9-BBN	70	47	18	0.4

Table 1. Catalytic reduction of CO₂ to methoxyborane R₂BOCH₃ as depict-

ed in Equation (1).

[a] Reaction time required to achieve a conversion of CO₂ into methoxyborane CH₃OBR₂ in a yield of greater than 90%. [b] The TON is calculated based on the formation of C–H bonds in CH₃OBR₂. [c] The TOF is calculated for the reaction time *t*.

33 h⁻¹. Hydrolysis of CH₃OBBN by using an excess of water and distillation of the resulting mixture under reduced pressure affords a solution of methanol in THF in quantitative yield (see the Experimental section). Monitoring the products distribution over time with ¹H and ¹³C NMR spectroscopic analysis reveals that CO₂ is rapidly consumed to yield the boryl formate derivative HCOOBBN (Figure 1). This first reduction step controls the kinetics of the transformation. Indeed, the formate species is



Figure 1. Distribution of the reduction products HCOOBBN, $H_2C(OBBN)_{2r}$ and CH₃OBBN (%) over time (min) for the catalytic reduction of CO₂ (1 bar) in the presence of (9-BBN)₂ (0.60 mol L⁻¹ in THF) and TBD (2.5 mol % with respect to the molar quantity of B–H functionalities).

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transient and does not accumulate in the reaction mixture because it is readily reduced to its acetal form $H_2C(OBBN)_2$. The latter is subsequently converted into methoxyborane. Interestingly, unlike **V**, which exhibits an induction period of several hours,^[10a] the formation of methoxyborane is observed within seconds after the reaction mixture is exposed to an atmosphere of CO₂ (Table 1, entries 8–23). The nature of the hydroborane species has only a minor influence on the catalytic activity of complex **III**, which promotes the reduction of CO₂ with pinBH, catBH, or 9-BBN with very similar TONs (i.e., 4–6 after 96 h at RT).^[8] Interestingly, the organocatalytic version of the reaction [Eq. (1)] depends on the reductant, and longer reaction times are needed to complete the reduction of CO₂ to methoxyborane when catBH is used in place of 9-BBN.



In fact, Me-TBD can promote the reduction of CO2 to CH₃OBcat with a TON of 54 (Table 1, entry 14,). In contrast, catBH is inert in the presence of CO₂, when DBU or TBD is used as a catalyst, even after 200 hours at 70 °C (Table 1, entries 15-18). Overall, the organocatalysts tested in Equation (1) proved to be competitive with the metal and organic catalysts depicted in Scheme 1, and although the systems developed by Guan and co-workers remain the most active catalysts, TBD, Me-TBD, and DBU exhibit a greater activity than the ruthenium and copper complexes II, III, and IV. Interestingly, TBD, 7methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (Me-TBD), and 1,8-diazabicycloundec-7-ene (DBU) are unreactive in the presence of BH₃·SMe₂, whereas this hydroborane species afforded the best results with the ambiphilic system $V^{[10a]}$ Yet, the use of V with 9-BBN gave a TON of 34 and a TOF of 12 h^{-1} at 70 $^\circ\text{C},$ relative to 648 and 33 h⁻¹, respectively, with Me-TBD at room temperature (Table 1, entry 12).

To comprehend the role of the organic catalyst better, the mechanism at play in the hydroboration of CO_2 was investigated with TBD as the catalyst and 9-BBN as the reductant. We recently demonstrated that guanidine TBD strongly binds to CO_2 to yield the stable adduct 1,^[12] which could be the starting step of the catalytic cycle. Reduction of a solution of 1 in THF with one equivalent of the (9-BBN)₂ dimer resulted in the immediate reduction of the activated CO_2 molecule at 25 °C. ¹H

and ¹³C NMR spectroscopic analysis of the crude mixture indicated the formation of a mixture of reduced species, among which the formate HCOOBBN and acetal $H_2C(OBBN)_2$ derivatives were identified [Eq. (2)].



Colorless crystals were deposited within hours from the reaction mixture. X-ray diffraction studies revealed the formation of a novel CO₂ adduct **2**, which formally results from the replacement of the acidic N–H proton in **1** with a BBN boryl group (Figure 2). Although **1** readily decarboxylates under reduced pressure, the CO₂ molecule is tightly bound to the guanidine–borane backbone in **2** and the adduct is stable even after 3 hours at 0.1 mbar at 25 °C. Structurally, the N1–C8 bond in **2** is shorter than in **1** (1.410(3) vs 1.480(3) Å, respectively), and the asymmetry in the C–O bond lengths is slightly more pronounced in **2** than in **1** (C8–O1: 1.299(3), C8–O2: 1.222(2) vs C8–O1: 1.257(3), C8–O2: 1.229(2) Å, respectively). Compound **2** can, therefore, be described

as an adduct between an intramolecular nitrogen/boron (N/B) FLP pair and CO_2 . Several examples of FLP– CO_2 adducts have been recently described by the groups of Stephan, Erker, Lam-



Figure 2. Molecular structure of **2** with displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1–C8: 1.410(3), C8–O1: 1.299(3), C8–O2: 1.222(2), O1–B1: 1.537(3); O1-C8-O2: 123.9(2).

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mertsma, and Tamm, and the reaction chemistry of these adducts was investigated in the presence of stoichiometric amounts of amine–boranes.^[13] Noticeably, these systems involve mostly phosphanes and N-heterocyclic carbenes (NHCs) as Lewis bases and only one nitrogen FLP has been reported for the activation of CO_2 .^[13a] This latter system resembles **2**, with a CO_2 molecule bound to an intramolecular amidine– borane FLP (N–C: 1.402(5) and B–O: 1.493(5) vs N–C: 1.410(3) and B–O: 1.537(3) Å, respectively, in **2**).

The reaction of TBD with 9-BBN was explored to rationalize the formation of the B–N bond in **2**. The addition of 9-BBN to a solution of TBD in THF affords adduct **3**, which was identified in situ by ¹H and ¹³C NMR spectroscopic analysis. Yet, **3** is unstable at room temperature and evolves into **4**, with the concomitant loss of H₂ (identified by ¹H NMR spectroscopy). By using this synthetic route, **4** was obtained in 75% yield of the isolated product after 1 hour at 70 °C [Eq. (3)] and was characterized by elemental and X-ray analyses (Figure 3). Compound



Figure 3. Molecular structure of 4 with displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1–B1: 1.601(2), N2_2–B1: 1.598(2), N1–C1: 1.3376(19), N2–C1: 1.3409(18), N3–C1: 1.3704(18); N1-C1-N2: 123.47(13).

4 directly results from the dimerization of the FLP responsible for the activation of CO_2 in **2**; therefore, the reaction chemistry of **4** with 9-BBN and CO_2 was investigated. Compound **4** reacts with 9-BBN at 100 °C to yield the borane adduct **5** in which the B–H bond of the incoming borane is activated by the N/B FLP system [Eq. (4) and Figure 4]. Similarly, exposing a solution of **4** in THF to an atmosphere of CO_2 leads to the formation of **2** in quantitative yield at 100 °C [Eq. (5)].



The chemical behavior depicted in Equations (4) and (5) clearly demonstrates that the dissociation of **4** is accessible to generate adducts. DFT calculations at the $M05-2X/6-31+G^*$

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Figure 4. Molecular structure of 5 with displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1–B1: 1.555(2), N2–B2: 1.550(2), C1–N1: 1.3434(19), C1–N2: 1.337(2), C1–N3: 1.3545(19); N1-C1-N2: 116.31(12).



Scheme 2. Computed pathway for the conversion of TBD into **2**, **4**, and **5** at the M05-2X/6-31 + G^* level of theory. The enthalpy and free energy associated with the dimerization of **TBD-BBN** to **4** was computed by replacing BBN with BMe₂ boryl groups (in **4** and **TBD-BBN**) on the energy surface.

level of theory indeed confirm that the formation of **4** from TBD and 9-BBN is exergonic ($\Delta G = -21.2 \text{ kcal mol}^{-1}$; Scheme 2). Nonetheless, the dissociation of **4** requires only 5.4 kcal mol⁻¹ and adducts **2** and **5** lie close in energy to **4** ($\Delta G = -24.2$ and $-20.7 \text{ kcal mol}^{-1}$, respectively; Scheme 2). Experimentally, both **2** and **5** promote the reduction of CO₂ and the treatment of **5** with an excess of CO₂ leads to the formation of **2** and a 2:3 mixture of H₂C(OBBN)₂ and CH₃OBBN after 21 hours at 70 °C [Eq. (6)].

4
$$\frac{CO_2, 1 \text{ bar}}{THF}$$
 2 + H₂C(OBBN)₂ + CH₃OBBN + BBNOBBN (6)
70 °C, 21 h >99% 32% 65%
(7) 4 + H₂C(OBBN)₂ + $\frac{0.5 (9-BBN)_2}{THF}$ 2 $\frac{+2 (9-BBN)_2}{BBNOBBN}$
23% 23% 70 °C, 30 min 70 °C, 8 h >99% >99%

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The reduction of the activated CO₂ molecule in 2 is somewhat faster. In fact, the addition of 0.5 equivalents of (9-BBN)₂ to a solution of 2 in THF leads to the formation of 5 and H₂C(OBBN)₂ in 23% yield after 30 minutes at 70°C, and the conversion of 2 into 5 and CH₃OBBN is complete within 8 hours at 70°C in the presence of 2 equivalents of (9-BBN)₂ [Eqs (7)and (8)]. The formation of the C^0 and C^{-II} products from the stoichiometric reactions depicted in Equations (6)-(8) strongly suggests that the guanidine-borane FLP system is active in the catalytic reduction of CO2. Indeed, 2 exhibits a catalytic activity identical to TBD for the reduction of CO₂ to methanol with 9-BBN (Table 1, entries 2 and 19). Compound 5 presents a somewhat lower catalytic activity (Table 1, entries 22 and 23) and requires about 84 hours at 25 °C to achieve complete reduction of CO₂. Interestingly, 5 was identified as the catalyst resting state at the end of the reaction performed with TBD or 2 (Table 1, entries 2, 8, 11, 19, and 20). Overall, these observations reveal that the guanidine-borane FLP forms under the applied reaction conditions and participates in the catalytic cycle.

The catalytic reduction of CO_2 to methoxyborane is kinetically controlled by the first hydroboration step, which yields the formoxyborane intermediate (Figure 1). The potential-energy surface of the catalytic hydroboration of CO_2 to HCOOBBN was computed at the DFT level to rationalize the experimental findings and identify the rate-determining states in the mechanism (the results are summarized in Scheme 3). In the absence of



Scheme 3. Computed pathway for the catalytic reduction of CO_2 with 0.5 equivalents of (9-BBN)₂ with catalyst 2 (at the M05–2X/6-31+G* level of theory). The labels in the boxes denote the compounds characterized experimentally (see the Experimental Section).

catalysts, the direct reduction of CO₂ to the boryl–formate derivative is exergonic ($\Delta G = -10.8 \text{ kcal mol}^{-1}$) and requires an activation energy of 30.2 kcal mol⁻¹. In contrast, the FLP-activated CO₂ molecule in **2** acts as a Lewis base to coordinate the incoming hydroborane species, and the resulting adduct **6** readily undergoes a hydride migration from the boron to the

carbon atom. The corresponding transition state TS₆₋₇ lies 27.7 kcalmol⁻¹ above the starting materials, thus demonstrating the positive influence of the catalyst on the reaction rates. Importantly, 5 does not form a stable adduct with CO₂, and a TS for the hydride transfer from 5 to CO₂ could not be located on the energy surface. This finding is in agreement with the lower reactivity of 5, for which the Lewis acidity of the boron center and the hydridicity of the borane are masked by coordination to the N/B FLP. Overall, the computed mechanism highlights the important role of the FLP system in increasing the nucleophilicity of the O centers in CO₂ while maintaining a high electrophilicity at the carbon atom. Indeed, the computed natural charge for the C center in 6 is +1.06, a value similar to that in free CO₂ ($q_{c} = +1.06$), whereas the charge at the O centers decreases from -0.53 in free CO_2 to -0.67 in $\boldsymbol{2}$ (-0.61 in 6). The ability of 2 to act as a Lewis base to activate the hydroborane reagent was confirmed experimentally by treating 2 with 0.5 equivalents of 9-BBNI [Eq. (9)].



The iodide anion is readily displaced by **2** to afford an unprecedented adduct **8**, in which the CO₂ molecule is activated by the guanidine function, namely, one borane and one boronium center (Figure 5). As such, the elongation of the C–O bond is more pronounced than in **2** (C8–O1: 1.268(2) and C8–O2: 1.257(2) Å) and the structural parameters are similar to those of the previously reported Mes₃P-CO₂-(AIX₃)₂ (X = CI, Br).^[13] Notably, **8** is also a unique example of a boronium cation stabilized by two activated CO₂ molecules, and the



Figure 5. Molecular structure of the cation in 8 with displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1–C8: 1.386(3), C8–O1: 1.268(2), C8–O2: 1.257(2), O1–B1: 1.566(3), O2–B2: 1.589(3); O1-C8-O2: 124.64(18).

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¹¹B NMR spectrum exhibits two resonances, in agreement with the presence of two aminoborane groups ($\Delta \delta$ = 4.2 ppm) and a boronium center ($\Delta \delta$ = 58.7 vs 3.9 ppm in **2**).^[14]

The mechanism for the reduction of CO₂ with 9-BBN catalyzed by Me-TBD was also investigated to determine the impact of replacing the N–H and N–B functionalities in TBD and **2** by an inert N–CH₃ linkage. Experimentally, Me-TBD does not react with CO₂.^[12] Yet, the addition of 0.5 equivalents of (9-BBN)₂ to a solution of Me-TBD in THF affords adduct **9**, which was characterized in solution by ¹H and ¹³C NMR spectroscopic analysis. Compound **9** promotes the reduction of CO₂ to the formate adduct **11** within minutes at 25 °C, and the formation of the C–H bond is supported by ¹H and ¹³C NMR spectroscopic analysis [Eq. (10)].



A mechanism similar to **2**, which relies on the activation of CO₂ by the guanidine catalyst, was first computed through DFT calculations (Scheme 4). The activation of CO₂ in this pathway requires the coordination of both Me-TBD and 9-BBN to yield adduct **12** (ΔG = +17.6 kcal mol⁻¹). Importantly, the CO₂ molecule in **12** is less electrophilic than in free CO₂, with



Scheme 4. Computed pathway (M05-2X/6-31 + G*) for the catalytic reduction of CO_2 to the formate derivative HCOOBBN, with Me-TBD, through the activation of CO_2 by using the quanidine catalyst.

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and 6. The subsequent hydride migration from the boron to the carbon atoms, therefore, requires a high activation energy of 40.6 kcalmol⁻¹, that is 10.4 kcalmol⁻¹ greater than the energy necessary for the uncatalyzed pathway (Scheme 4). As a result, an alternative pathway was computed to account for the catalytic activity of Me-TBD. In agreement with Equation (10), the addition of (9-BBN)₂ to Me-TBD leads to the formation of the stable adduct 9. Coordination of the lone pair of electrons on the nitrogen atom to the vacant orbital in the boron atom results in an increase of the B-H-bond polarity and a decrease in the $q_{\rm H}$ value from +0.16 in free 9-BBN to -0.05 in **9** upon coordination (in parallel, the $q_{\rm B}$ value increases slightly from +0.35 to +0.36). This activation of the hydroborane species is efficient and leads to the reduction of CO₂ with a low energy barrier of 23.8 kcal mol⁻¹ via TS_{9-10} (Scheme 5). The resulting ion pair 10 readily converts into the more stable 11 after nucleophilic attack of the formate anion onto the electrophilic boron center, as expected from Equation (10). Me-TBD is then released by de-coordination of HCO₂BBN to close the catalytic cycle.

a carbon charge of $q_{\rm C} = +0.99$ relative to +1.06 in both CO₂



Scheme 5. Computed pathway (M05-2X/6-31 + G*) for the catalytic reduction of CO₂ to the formate derivative HCOOBBN, with Me-TBD, through the activation of 9-BBN by using the guanidine catalyst. The labels in the boxes denote the compounds characterized experimentally (see the Experimental Section).

Overall, TBD and Me-TBD follow two distinct mechanisms that are both efficient in the catalytic hydroboration of CO_2 (Scheme 6). Under the applied reaction conditions, TBD is converted into an N/B FLP system that can promote the activation of CO_2 by increasing the nucleophilicity of the O atom while maintaining the partial positive charge on the C center (**6**). This mechanism is similar to the reaction pathway proposed by Fontaine and co-workers for the hydroboration of CO_2 promoted by **V**, although the authors did not compute any transition state.^[10a] In contrast, Me-TBD preferentially activates the







Scheme 6. Schematic pathways for the catalytic hydroboration of CO_2 to formoxyborane HCOOBR₂ with TBD and **6** (left) or Me-TBD (middle) as the catalysts. The activation energies (in THF) are summarized (right) for the reduction of CO_2 to the formate derivative HCOOBR₂ with 9-BBN and catBH as the reductants for the different mechanisms.

hydroborane species by increasing its hydridic character. Because DBU lacks any N-H functionality, it is likely that this amidine catalyst follows a reaction path similar to Me-TBD. The rate-determining state of highest energy is the transition state that results in the formation of the C-H bond in both mechanisms (Scheme 6). Because these transition states lead to the formation of zwitterions or ion pairs, their energy is better described by taking into account the influence of the solvent. The energy demand for each pathway was, therefore, computed by means of a polarizable continuum model (PCM) for the THF solvation (Scheme 6, right-hand side). The influence of the polar solvent has only a minor impact on the hydroboration of CO₂ catalyzed by 6 because the two rate-determining states have a similar polarity. The activation energy for **6** ($\Delta G_1^{\# 9\text{-BBN}} =$ 30.1 kcalmol⁻¹) is only slightly favored relative to the uncatalyzed reaction ($\Delta G = 30.8 \text{ kcal mol}^{-1}$). Notably, the transition state TS_2^{9-BBN} that corresponds to the reduction of CO_2 promoted by Me-TBD is strongly facilitated by the polar solvent because it connects the neutral starting materials with an ion pair (i.e., 10). As such, Me-TBD lowers the activation energy for the conversion of CO₂ into formoxyborane to $\Delta G_2^{\# 9-\text{BBN}} =$ 10.6 kcal mol⁻¹ (Scheme 6). These results also explain the difference in reactivity between TBD and Me-TBD when catBH is used as the reductant. Indeed, catBH has a lower acidity than 9-BBN and its utilization is more efficient in a pathway that involves the direct activation of the reductant by Me-TBD. Computationally, the activation energy of $\Delta G_1^{\text{table}} = 33.4 \text{ kcal mol}^{-1}$ required for the reduction of CO₂ with catBH and TBD is incompatible with catalytic activity. Nonetheless, Me-TBD promotes the hydroboration of CO₂ with an energy demand of 16.5 kcal mol⁻¹, in line with the catalytic results (Table 1, entry 14).

Conclusion

We have described herein the first nitrogen bases able to promote the catalytic hydroboration of CO₂. Reactive hydroboranes include 9-BBN and catBH and enable the reduction of CO₂ to the methoxide level. Guanidine and amidine derivatives, such as TBD, Me-TBD, and DBU, proved to be active catalysts for this transformation and Me-TBD catalyzes the reduction of CO₂ to methoxyborane at room temperature with TONs and TOFs of up to 648 and 33 h^{-1} (25 °C), respectively. Formate HCOOBR₂ and acetal H₂C(OBR₂)₂ derivatives were identified as reaction intermediates in the reduction of CO₂ with R₂BH and the first C-H-bond formation is rate determining. Experimental and computational investigations showed that TBD and Me-TBD follow different mechanisms. Although Me-TBD promotes the reduction of CO₂ through the activation of the hydroborane reagent and formation of ion pairs, TBD is converted into an N/B frustrated Lewis pair that activates CO₂ and facilitates the hydride transfer from the boron to the carbon atom. Current efforts are devoted to translating these conclusions into the design of new efficient catalysts that combine supplementary coordination sites for the activation of the hydroborane moiety and CO₂.

Experimental Section

General considerations

All the reactions and manipulations were performed at 20 $^{\circ}$ C in a recirculating mBraun LabMaster DP inert-atmosphere (Ar) drybox and with vacuum Schlenk lines. Glassware was dried overnight at 60 $^{\circ}$ C before use. ¹H and ¹³C NMR spectra were obtained by using a Bruker DPX 200 MHz spectrometer. ¹¹B NMR spectra were ob-

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tained by using a Bruker Avance 400 MHz spectrometer. Chemical shifts for ¹H and ¹³C{¹H} NMR spectra were referenced to solvent impurities. Chemical shifts for ¹¹B NMR spectra were referenced by using Et₂O·BF₃ as an external standard. Elemental analyses were performed at the CNRS facility in Gif-Sur-Yvette (France). Unless otherwise noted, reagents were purchased from commercial suppliers and dried over molecular sieves (4 Å) prior to use. The molecular sieves (4 Å; Aldrich) were dried under a dynamic vacuum at 250 °C for 48 h prior to use. THF, [D₆]THF, toluene, pentane, and [D₆]benzene were dried over a sodium(0)/benzophenone mixture and distilled before use. CD₃CN and CD₂Cl₂ were dried over CaH₂ and distilled before use. Carbon dioxide was purchased from Messer in a 5.5 purity gas bottle.

Computational details

The M05-2X functional was employed to optimize the equilibrium molecular structure of the model compounds. This functional was specifically developed to describe organic systems with nonbonding interactions and proved to be efficient and reliable for investigating reaction mechanisms. The $6-31+G^*$ sets were used for the carbon, hydrogen, nitrogen, oxygen, and silicon atoms, except for the carbon atom of the CO₂ pattern and the hydride moiety of the borane pattern, which were described by using $6-311 + +G^{**}$ as the basis. All the geometries were fully optimized without any symmetry or geometry constrains. Harmonic vibrational analyses were performed to confirm and characterize the structures as minima or transition states. The vibrational data were used to relax the geometry of each transition state toward the reactants and products to confirm its nature. Free energies were calculated within the harmonic approximation for vibrational frequencies. The effect of the THF solvent on the energy demand for each pathway was evaluated through single-point calculations with the polarizable-continuum model (PCM). All the calculations were carried out by using the Gaussian09 suite of codes.^[15]

Synthesis

2: A 20 mL round-bottom flask equipped with a stirring bar and a J. Young valve was charged with 4 (71.0 mg, 0.14 mmol) and THF (4 mL). The reaction mixture was exposed to a CO₂ atmosphere (1 bar), and the flask was sealed and heated to 100 $^\circ C$ for 75 min. The reaction mixture was cooled to room temperature, and the volatiles were removed under reduced pressure to afford 2 as a white solid (83.0 mg, 0.14 mmol, 100%). X-ray-quality samples of 2 were obtained in an NMR tube by diffusion of pentane into a solution of **2** in THF. ¹H NMR ([D₈]THF, 298 K): $\delta = 3.69$ (pseudo-t, 2H; CH₂ TBD), 3.53 (pseudo-t, 2H; CH₂ TBD), 3.39-3.25 (m, 4H; CH₂ TBD), 2.13–1.29 (m, 16 H), 0.69 ppm (br s, 2 H); ^{13}C NMR ([D_g]THF, 298 K): $\delta = 152.4$ (OCO), 151.1 (NCN₂), 49.3 (CH₂), 48.4 (CH₂), 44.3 (CH₂), 41.7 (CH₂), 33.1 (CH₂), 32.7 (CH₂), 25.4 (CH), 22.3 (CH₂), 22.2 ppm (CH₂); ¹¹B NMR ([D₈]THF, 298 K): $\delta = 3.3$ ppm (brs, 1B); ¹H NMR (CD₂Cl₂, 298 K): $\delta = 3.73$ (pseudo-t, 2H; CH₂ TBD), 3.54 (pseudo-t, 2H; CH₂ TBD), 3.30-3.23 (m, 4H; CH₂ TBD), 2.03-1.65 (m, 12 H), 1.56-1.41 (m, 4 H), 0.69 ppm (brs, 2 H); ¹³C NMR (CD₂Cl₂, 298 K): $\delta = 153.1$ (OCO), 150.2 (NCN₂), 49.0 (CH₂), 48.2 (CH₂), 43.7 (CH₂), 41.5 (CH₂), 32.5, 32.0, 24.7, 24.6, 21.7(1) (CH₂), 21.6(8) ppm (CH₂); ¹¹B NMR (CD₂Cl₂, 298 K): δ = 3.9 ppm (brs); elemental analysis (%) calcd for C₁₆H₂₆BN₃O₂ (303.21): C 63.38, H 8.64, N 13.86; found: C 63.20, H 8.78, N 13.89.

Formation in situ and characterization of 3: A 2.5 mL NMR tube equipped with a J. Young valve was charged with TBD (16.7 mg, 0.12 mmol, 1 equiv), (9-BBN)₂ (14.6 mg, 0.06 mmol, 0.5 equiv), and $[D_{a}]THF$ (0.5 mL) to form **3** (quant.), which was identified by its ¹H

and ¹³C{¹H} NMR spectra in [D₈]THF. ¹H NMR ([D₈]THF, 298 K): δ = 6.29 (brs, 1 H; NH TBD), 3.36 (pseudo-t, 2 H; CH₂ TBD), 3.28–3.15 (m, 6 H; CH₂), 1.96–1.40 (m, 17 H), 0.80 ppm (brs, 2 H); ¹³C NMR ([D₈]THF, 298 K): δ = 152.2 (NCN₂), 48.1 (CH₂), 43.1 (CH₂), 39.3 (CH₂), 37.0 (CH₂), 31.4, 26.1, 25.9, 23.1, 22.6 ppm (CH₂).

4: A 20 mL round-bottom flask equipped with a stirring bar and a J. Young valve was charged with TBD (163.1 mg, 1.17 mmol, 1 equiv), (9-BBN)₂ (143.0 mg, 0.590 mmol, 0.5 equiv), and THF (3.5 mL). The flask was sealed, and the reaction mixture was stirred for 1 h at 70 °C, thus leading to the formation of a white solid. The reaction mixture was cooled to room temperature, and the precipitate was recovered by filtration. The resulting solid is washed with Et₂O (3×5 mL) and dried under reduced pressure to afford **4** (226.0 mg, 0.436 mmol, 75%). X-ray-quality samples of **4** were obtained in an NMR tube by cooling a solution of **4** in THF from 100 to 25 °C. Note: the insolubility of **4** at room temperature in THF, Et₂O, pentane, benzene, acetonitrile, CH₂Cl₂, and pyridine precluded the recording of meaningful ¹H, ¹³C, or ¹¹B NMR spectroscopic data. Elemental analysis (%) calcd for C₃₀H₅₂B₂N₆ (518.40): C 69.51, H 10.11, N 16.21; found: C 69.43, H 10.22, N 16.33.

5: A 20 mL round-bottom flask equipped with a stirring bar and a J. Young valve was charged with 4 (100.0 mg, 0.190 mmol, 1 equiv), (9-BBN)₂ (51.0 mg, 0.210 mmol, 1.1 equiv), and THF (5 mL). The flask was sealed, and the reaction mixture was stirred for 150 min at 100 °C. The mixture was cooled to room temperature and concentrated down to 2 mL. A white solid formed during the evaporation of the solvent. The resulting solid was washed with Et_2O (3×5 mL) and dried under reduced pressure to afford 5 (110.5 mg, 0.290 mmol, 76%). X-ray-quality samples of 5 were obtained in an NMR tube by cooling a solution of 5 in THF from 100 to 25 °C. ¹H NMR ([D₈]THF, 298 K): δ = 3.41 (pseudo-t, 4H; CH₂ TBD), 3.34-3.12 (m, 4H; CH₂ TBD), 2.11-1.36 (m, 29H; CH₂), 1.02 ppm (brs, 4H; CH BBN); ^{13}C NMR ([D_8]THF, 298 K): $\delta\!=\!157.3$ (NCN_2), 48.4 (CH_2) , 44.5 (CH_2) , 33.1 (CH_2) , 25.9 (CH_2) , 25.6 (CH), 24.0 ppm (CH_2) ; ¹¹B NMR ([D₈]THF, 298 K): $\delta = 12.8$ ppm (brs); elemental analysis (%) calcd for $C_{23}H_{41}B_2N_3$ (381.21): C 72.46, H 10.84, N 11.02; found: C 71.85, H 10.88, N 10.69.

8: A 20 mL round bottom-flask equipped with a stirring bar and a J. Young valve was charged with **2** (30.0 mg, 0.099 mmol, 1 equiv), B-iodo-9-BBN solution in hexanes (50 µL, 1 m, 0.050 mmol, 0.51 equiv), and toluene (1.5 mL). The flask was sealed, and the reaction mixture was stirred for 30 min at room temperature, thus leading to the formation of a white precipitate. The solid was recovered by filtration, washed with pentane (3×5 mL), and dried under reduced pressure to afford **8** (85%). ¹H NMR (CD₂Cl₂, 298 K): δ = 3.58 (pseudo t, 4H; CH₂ TBD), 3.66–3.44 (m, 12H; CH₂ TBD), 2.14–1.45 (m, 44H), 1.14 (brs, 2H), 0.71 ppm (brs, 4H); ¹³C NMR (CD₂Cl₂, 298 K): δ = 157.7 (OCO), 148.8 (NCN₂), 50.0 (CH₂), 44.6 (CH₂), 44.1 (CH₂), 33.7, 33.5, 32.2, 31.9, 31.5, 24.5, 24.2, 23.9, 23.5, 22.6 (br), 21.2, 20.8 ppm; ¹¹B NMR (CD₂Cl₂, 298 K): δ = 58.7 (brs, 1B), 4.2 ppm (brs, 2B).

Formation in situ and characterization of 9 and 11: A 2.5 mL NMR tube equipped with a J. Young valve was charged with Me-TBD (16.9 mg, 0.11 mmol, 1 equiv), (9-BBN)₂ (13.5 mg, 0.055 mmol, 0.5 equiv), and [D₈]THF (0.5 mL). Compound 9 was formed quantitatively and identified by its ¹H and ¹³C{¹H} NMR spectra in [D₈]THF. The reaction mixture was exposed to an atmosphere of CO₂ (1 bar) to yield 11, which was identified by its ¹H and ¹³C{¹H} NMR spectra in [D₈]THF.

9: ¹H NMR ([D₈]THF, 298 K): δ = 3.33–3.13 (m, 6 H; CH₂ MTBD), 3.08 (pseudo-t, 2 H; CH₂ MTBD), 3.01 (s, 3 H; CH₃), 2.03–1.31 (m, 17 H), 0.80 ppm (br s, 2 H); ¹³C NMR ([D₈]THF, 298 K): δ = 159.4 (NCN₂), 48.7

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(CH₂), 48.3 (CH₂), 48.2 (CH₂), 43.2 (CH₂), 40.2 (CH₃), 36.6 (CH₂ BBN), 31.2 (1C), 26.8, 26.1, 25.8, 23.0 ppm.

11: ¹H NMR ([D₈]THF, 298 K): δ = 8.33 (s, 1H; HCOO), 3.52–3.12 (m, 8H; CH₂ MTBD), 3.06 (s, 3H; CH₃), 2.14–1.32 (m, 16H), 1.06 ppm (b sr, 2H); ¹³C NMR ([D₈]THF, 298 K): δ = 163.6 (HCOO), 161.5 (NCN₂), 48.7 (CH₂), 48.3 (CH₂), 47.8 (CH₂), 42.3 (CH₃), 42.1 (CH₂), 32.6 (CH₂), 26.8, 25.1, 22.4 ppm.

Typical procedure for the catalytic hydroboration of CO₂ to methanol: The typical procedure is detailed for the conversion of CO₂ into methanol with TBD as the catalyst and (9-BBN)₂ as the reductant (Table 1, entry 2). A 2.5 mL NMR tube equipped with a J. Young valve was charged with TBD (1.7 mg, 0.012 mmol, 0.050 equiv), (9-BBN)₂ (58.6 mg, 0.240 mmol, 1.00 equiv), and [D₈]THF (0.40 mL). The reaction mixture was exposed to an atmosphere of CO₂ (1 bar), and the flask was sealed. The formation of CH₃OBBN was followed by ¹H NMR spectroscopic analysis in [D₈]THF with Ph₂CH₂ as an internal standard. Selected ¹H and ¹³C NMR spectroscopic data ([D₈]THF) for: HCOOBBN (δ = 8.24 (HCOO) and 163.2 ppm (HCOO)), $H_2C(OBBN)_2$ ($\delta = 5.54$ ($H_2C(OBBN)_2$) and 86.5 ppm (H₂C(OBBN)₂)), and CH₃OBBN (δ = 3.71 (CH₃OBBN) and 53.4 ppm (CH₃OBBN)). When full conversion of CO₂ was achieved (CH₃OBBN; 0.114 mmol, 1.00 equiv), H₂O (20 μL, 1.1 mmol, 10 equiv) was added to the reaction mixture. The reaction mixture is distilled after 1 h under reduced pressure to afford a solution of methanol in THF (0.105 mmol, 0.921 equiv, 92%). The formation of methanol was determined by using ¹H NMR spectroscopy with [D₈]THF as the solvent and Ph₂CH₂ as an internal standard.

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FULL PAPER

Organocatalysis

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Metal-Free Reduction of CO₂ with Hydroboranes: Two Efficient Pathways at Play for the Reduction of CO₂ to Methanol



Highly efficient metal-free catalysis for the reduction of CO_2 to methanol with hydroboranes as the reductant and guanidines and amidines as the catalyst (see picture). Experimental and DFT results show that the reaction proceeds through two different pathways depending on the nature of the organocatalyst.