Catalytic CO$_2$ Reduction with Boron- and Aluminum Hydrides

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The previously reported dimeric NHI aluminum dihydrides **1 a,b**, as well as the bis(NHI) aluminum dihydride salt **9**$^+$[OTs]$^-$, the bis(NHI) boron dihydride salt **10**$^+$[OTs]$^-$, and the "free" bis(NHI) ligand **12** were investigated with regard to their activity as a homogenous (pre)catalyst in the hydroboration (i.e. catalytic reduction) of carbon dioxide (CO$_2$) in chloroform under mild conditions (i.e. room temperature, 1 atm; NHI=N-heterocyclic imine, Ts=tosyl). Borane dimethylsulfide complex and catecholborane were used as a hydride source. Surprisingly, the less sterically hindered **1 a** exhibited lower catalytic activity than the bulkier **1 b**. A similarly unexpected discrepancy was found with the lower catalytic activity of **10**$^+$ in comparison to the one of the bis(NHI) **12**. The latter is incorporated as the ligand to the boron center in **10**$^+$. To elucidate possible mechanisms for CO$_2$ reduction the compounds were subjected to stoichiometric reactivity studies with the borane or CO$_2$. Aluminum carboxylates **4**, **6**, and **7**$^+$ with two, four, and one formate group per two aluminum centers were isolated. Also, the boron formate salt **11**$^+$[OTs]$^-$ was characterized. Selected metal formates were subjected to stoichiometric reactions with boranes and/or tested as a catalyst. We conclude that each type of catalyst (**1 a,b**, **9**$^+$, **10**$^+$, **12**) follows an individual mechanistic pathway for CO$_2$ reduction.

Nowadays, a chemical transformation of outstanding importance to the biosphere is the catalytic reduction of carbon dioxide. The massive amounts produced by combustion of fossil fuels are commonly acknowledged to promote climate change and sea-water acidification.[1] Hence, it is paramount to transform the greenhouse gas back to organic feedstock materials. This requires the use of efficient catalysts which should be environmentally benign to prevent additional stress on the ecosystem. In recent times, research in the fields of lighter main group metal(loid) catalysis[2] and organocatalysis[3] has produced systems that are less harmful to the environment and also contain less monetary expensive materials than comparable transition metal catalysts.

A wide scope of transition metal-based catalysts has been established for the (photo/electro)catalytic reduction of CO$_2$.[4] A few years ago, the number of studies on organocatalytic CO$_2$ transformations, particularly with regard to hydrogenation/reduction, started to surge.[4b,f,5] Here, strong Brønsted/Lewis bases as N-heterocyclic carbenes (NHC, **A**) or triazabicyclodecenes (**B**, TBD) are typically implemented to promote chemical reduction of CO$_2$ (Figure 1). In recent times, electron-precise
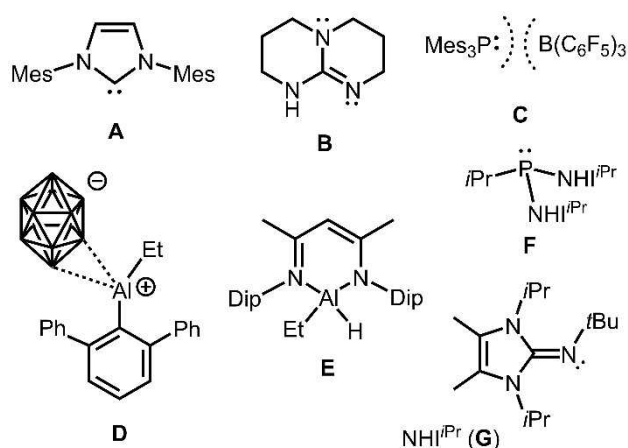

Figure 1. Typical examples for strong Lewis base organocatalysts NHC (**A**) and TBD (**B**). The frustrated Lewis Pair metal-free catalyst **C**. The cationic aluminum complex **D** and the 1,3-diketimino aluminum hydride **E**. The potent Lewis bases **F** and **G** for reversible CO$_2$ binding that are both based on N-heterocyclic imine (NHI). Mes=mesityl, Dip=2,6-diisopropylphenyl, icosahedron=CHB$_{11}$Cl$_{11}$.

complexes of s- and p-block metal(loid)s have made a similar upcoming for catalytic CO$_2$ reduction.[6] Similarly, Frustrated Lewis Pairs (**C**, FLP) have also been used as catalysts for this type of transformation.[7] A number of aluminum cations (**D**) reported by Wehmschulte and coworkers and a non-ionic catalytic system based on boron- and aluminum Lewis acids are to be pointed out, as well (Figure 1).[6a,d,8]

More recently, our group and others have reported the hydroboration of carbonyl functionalities promoted by aluminum hydride complexes as catalysts (Figure 2).[9] The successful implementation of this type of compounds for the catalytic

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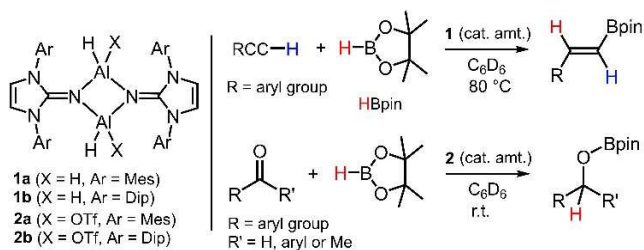
Figure 2. Examples (former work) for catalytic hydroboration of terminal alkynes (top) and carbonyl compounds (bottom) using imino aluminum hydrides (**1**, **2**).

Table 1. Results on catalytic hydroboration/reduction of CO_2 with borane dimethylsulfide complex using NHI-based catalysts.

Entry	cat. (mol%)	Time	Yield
1	**1a** (5%)	1 h	25%
		3 h	53%
		6 h	77%
		24 h	87%
2	**1b** (5%)	1 h	63%
		3 h	98%
		≤ 6 h	99+%
3	**9**[+][OTs][−] (4%)	1 h	6%
		3 h	n.a.
		6 h	12%
		24 h	22%
4	**10**[+][OTs][−] (5%)	1 h	28%
		3 h	52%
		6 h	76%
		≤ 24 h	99+%
5	**12** (5%)	1 h	90%
		≤ 3 h	99+%

Remarks: Solutions (ca. 1 molar) of $H_3B \cdot SMe_2$ in $CDCl_3$ with (pre)catalyst (5 or 4 mol%, $^5/_3$ or $^4/_3$ mol% normalized to active hydride) in CO_2 atmosphere (1.0–1.1 bar) at room temperature (20-25 °C). NMR samples drawn under CO_2 atm. at indicated reaction time and filled under N_2 atm. (no degassing). Data recorded approx. 30 min after filling. Yield of "MeO" determined by relative intensities (^1H NMR) of alkoxy to SMe_2 signals.

reduction of CO_2 has, however, not been described. In 2018, the group of Aldridge outlined the reactivity of 1,3-diketimino aluminum hydride (**E**) and selected derivatives with CO_2, catecholborane and borane dimethylsulfide complex (Figure 1).[10] The authors did not detail the use of their aluminum hydrides for a catalytically driven CO_2 reduction. Notably, reactivity studies on a very similar but less sterically congested aluminum hydride with CO_2 were presented very recently but also no catalytic process was described.[11] In the context of CO_2 transformations with aluminum complexes a study of Myers and Berben on catalytic dehydrogenation of formic acid to CO_2 and H_2 is particularly noteworthy.[12]

Our ongoing interest in group 13 metal(loid) hydrides bearing an N-heterocyclic imino (NHI) group[13] as a ligand has prompted us to examine the utility of such NHI compounds as main group element catalysts for the hydroboration (i.e. reduction) of CO_2. These compounds have been part of previous studies.[9b,14] Notably, organic superbases containing the NHI group have been described to reversibly bond to CO_2 (**F**, **G**, Figure 1).[15]

Recently, we described the catalytic hydroboration of terminal alkynes and of carbonyl compounds (e.g. aldehydes and ketones) with pinacolborane using NHI aluminum hydrides as catalysts (Figure 2).[9b] Accordingly, we exposed a solution of pinacolborane in $CDCl_3$ to an atmosphere of CO_2 (1.0–1.1 bar) in the presence of catalytic amounts (1–5 mol%) of **1** or **2**. No notable conversion of the hydridoborane was recognized. Even when heating a reaction setup containing **1b** as a (pre)catalyst to 60 °C for several hours

just traces of desired methoxyborane were detected via ^{11}B NMR analysis. This agrees with the generally lower susceptibility of CO_2 towards hydroboration because the second oxygen atom as a highly electronegative entity renders the C=O bond less electron-rich than the one in aldehydes or ketones. Thus, we switched to borane dimethylsulfide complex as a reductant which is commonly known to be a stronger hydroboration reagent than pinacolborane. In the outcome, major transformation of CO_2 into methoxyborane equivalents was observed within hours at ambient temperature using **1** as a catalyst (Table 1). Surprisingly, the less congested aluminum hydride (**1a**) exhibited decreased catalytic activity as compared to the bulkier **1b** (Table 1, Entries 1 and 2). With regard to mechanistic investigations one must note that the reaction of

1b with $H_3B \cdot SMe_2$ (4 equivalents) had been reported to yield the aluminum borohydride **3** (Scheme 1).[14c] In $CDCl_3$ solution **3** does not convert when exposed to an atmosphere of CO_2 which indicates that initial reaction between **1b** and the borane is not a viable pathway for the concerned catalytic reduction. In contrast, a solution of **1b** in $CDCl_3$ quantitatively reacts with CO_2 (1 atm) within 2 hours to yield the dicarboxylate **4** (Scheme 1). The presence of two O(CO)H groups (i.e. formate) is confirmed by a singlet at 6.98 ppm in the ^1H NMR spectrum ($CDCl_3$) with 2H relative intensity. Also, we obtained a single crystal of **4** that was determined to the diformate by XRD analysis with the formate groups at the four-membered ring in *trans*-position relative to each other (Figure 3). After exposure of the less hindered congener **1a** in $CDCl_3$ to CO_2 for 38 h the tetracarboxylate **6** was isolated (Scheme 1). A proton resonance at 7.32 ppm integrates to 4H indicating the introduction of four O(CO)H groups and this structural formulation was also confirmed by SCXRD study (Figure 4). The formation of the respective dicarboxylate could not be observed by NMR spectroscopy and it is believed to be elusive under these conditions. Notably, bulkier **4** dissolved in $CDCl_3$ transforms into a tetracarboxylate species when kept in a CO_2 atmosphere for an additional period of 8 days (Scheme 1). This reduced susceptibility of the "second" hydride at the aluminum center for CO_2 insertion is in agreement with the finding that $CDCl_3$ solutions of the bistriflates **2a** and **2b** do not react with CO_2 on a 1 to 5 days timescale.
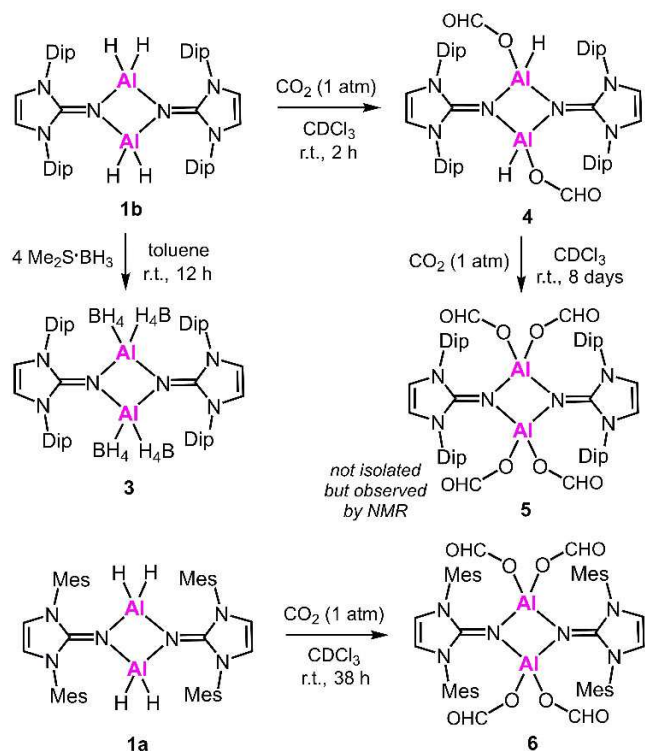
Scheme 1. Synthesis of the aluminum borohydride 3 and the aluminum carboxylates 4–6 (Dip = 2,6-diisopropylphenyl, Mes = mesityl).
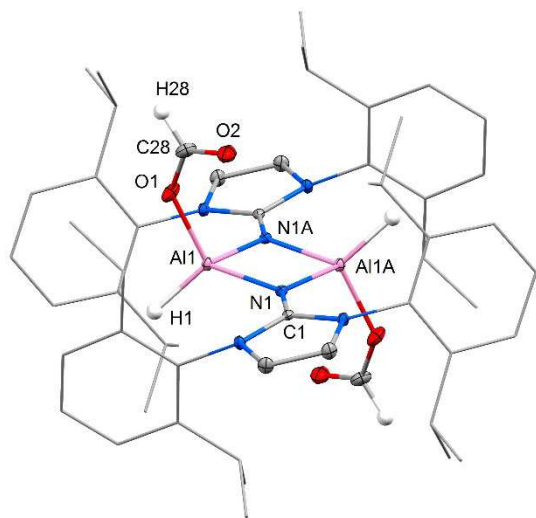

Figure 3. Molecular structure of 4 in the solid state as derived from SCXRD analysis (thermal ellipsoids are depicted at the 30% level). Dip groups are depicted as wireframe model. Hydrogen atoms omitted except at Al and formate. Selected bond lengths [Å], angles [°], and atom⋯atom distance [Å]: Al1-O1 = 1.785(1), Al1-N1 = 1.882(1), Al1-N1A = 1.891(1), O1-C28 = 1.287(2), O2-C28 = 1.201(2), N1-C1 = 1.305(2); N1-Al1-N1A = 86.6(1), Al1-N1-Al1A = 93.4(1), O1-C28-O2 = 128.8(1); Al⋯Al = 2.746(1).

With the elucidation of mechanistic pathways for CO_2 reduction and boron-oxygen bond formation in mind, we investigated the formate group transfer capability of the

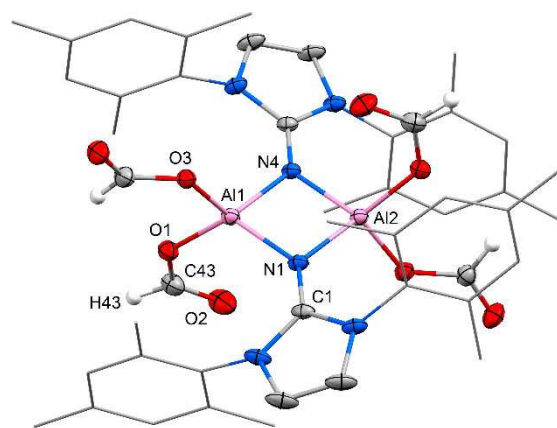Figure 4. Molecular structure of 6 in the solid state as derived from SCXRD analysis (thermal ellipsoids are depicted at the 30% level). Mesityl groups are depicted as wireframe model. Hydrogen atoms omitted except at formate. Selected bond lengths [Å], angles [°], and atom⋯atom distance [Å]: Al1-O1 = 1.769(2), Al1-O3 = 1.777(1), Al1-N1 = 1.859(2), Al1-N4 = 1.863(2), O1-C43 = 1.294(3), O2-C43 = 1.209(3), N1-C1 = 1.319(2); N1-Al1-N4 = 87.6(1), O1-Al1-O3 = 101.5(1), Al1-N1-Al2 = 92.5(1), O1-C43-O2 = 125.9(2); Al⋯Al = 2.689(1).

aluminum carboxylate **4**. The reactions with the strong Lewis acids Ph_3C^+ (cationic, used as $Ph_3C^+[Al(OR^F)_4]^-$) and $B(C_6F_5)_3$ (uncharged) in $CDCl_3$ solution were probed in an NMR sample tube (Scheme 2, $R^F = C(CF_3)_3$). The trityl salt afforded a clean conversion to a new NHI species (^{1}H NMR spectroscopic control) upon reaction in a one-to-one ratio. In contrast, two equivalents of $B(C_6F_5)_3$ were required until the signal pattern of the proton resonances produced by the NHI ligand matched the ^{1}H NMR spectrum of the trityl salt conversion of **4**. A singlet at 7.69 ppm integrates to 1H and is assigned to a formate group which resonates at significantly lower field as the carboxylate groups in **4** or **6**. Also, the formation of triphenylformylmethane and of the $[HCO_2(B(C_6F_5)_3)_2]^-$ anion, respectively, is concluded from [1]H
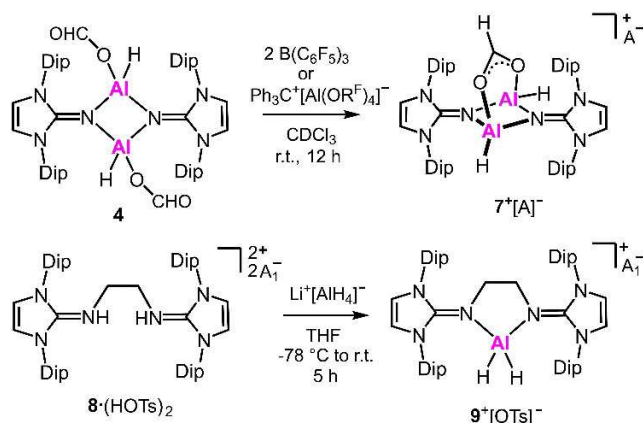
Scheme 2. Syntheses of the cationic aluminum complexes **7⁺** and **9⁺** via formate group abstraction from **4** or dehydrogenative coupling between **8**·[HOTs]₂ and $Li^+[AlH_4]^-$ (A = $HCO_2(B(C_6F_5)_3)_2$ or $Al(OR^F)_4$, A₁ = OTs; Dip = 2,6-diisopropylphenyl, Ts = tosyl, $R^F = C(CF_3)_3$).

and ^{11}B NMR analysis. As the ^1H NMR spectrum of 7^+ in $CDCl_3$ suggests high symmetry for the complex we surmise the single formate group to assume a bridging position between the aluminum centers decorating the four-membered Al_2N_2 ring. Consequently, we postulate the structural formulation 7^+ (Scheme 2). This is confirmed via SCXRD analysis (see the SI, Figure S39). It is of note that the potential to assume an intramolecular carboxylate-bridge structure motif as in 7^+ should result in markedly different formate group donor strengths of dinuclear aluminum complexes as **4** in comparison to formates derived from mononuclear aluminum compounds of type **E**.

In order to further elucidate the mechanism for CO_2 reduction we brought **4**, as well as **6** into contact with $H_3B \cdot SMe_2$ (3 and 6 equiv, respectively) in $CDCl_3$ in an NMR sample tube. Monitoring the progress of the reaction revealed the formation of an untraceable mixture of NHI ligand species in the ^1H NMR in both cases (see the SI, Figures S21, S23, S25, S27). Counterintuitive to the expectation from the steric properties the bulkier **4** had decomposed completely within one hour while the less congested **6** was still observed as the major component within the same timeframe though the latter was exposed to a larger excess of the borane (7 h later **6** was found to have quantitatively disintegrated). The decomposition rates of **4** and **6** correlate to the catalytic activities of **1b** and **1a** for which bulkier **1b** was also found to exhibit the higher CO_2 conversion rate (Table 1, Entries 2 and 1). It is also to be noted that in the case of the conversion of **4** with $H_3B \cdot SMe_2$ the ^{11}B NMR analysis (after 5 h elapsed) showed two broad resonances (-37 ppm, -40 ppm) and a sharp quintet of weaker intensity (-41.5 ppm, $J = 81$ Hz; note: residual $H_3B \cdot SMe_2$ was observed at -20.4 ppm, see the SI, Figures S22, S24). The -37 ppm signal is in agreement with the value reported for the aluminum borohydride **3** while the most upfield shifted resonance can clearly be assigned to $[BH_4]^-$. Such resonances were found in the ^{11}B spectrum of the conversion of **6** with excess borane, however, aside from the far slower conversion rate the relative intensity of the $[BH_4]^-$ signal was considerably increased and only traces of the two broader resonances were shown (see the SI, Figures S26, S28). The formation of $[BH_4]^-$ is of particular interest because traces of $Na[BH_4]$ had been reported to catalyze the reduction of CO_2 to trimethoxyboroxine with $H_3B \cdot thf$ in THF.[16]

The reactivity towards carboxylate group acceptor reagents (i.e. synthesis of 7^+) shows that dimeric aluminum complexes of type **4** may readily act as carboxylate group transfer agents. However, after consideration of the reaction profile of **4** towards excess $H_3B \cdot SMe_2$ (vide supra) we do not propose that the respective complex 7^+ constitutes a relevant intermediate in the reduction of CO_2 with this borane and **1b** as a precatalyst. Taking into account the conversions described above we conclude that the catalytic CO_2 reduction with **1** commences with insertion of CO_2 into the Al–H bonds rather than initial reaction with the borane because a resulting complex of type **3** would be an ending path. It is conceivable, however, that a mixed $Al(H)BH_4$ species promotes CO_2 reduction but its existence could not be verified albeit the assigned ^{11}B NMR

signal at -40 ppm from conversions of **4** or **6** with excess borane (vide supra) could be produced by such type of complex. Nevertheless, the absence of CO_2 insertion to occur for **2** and **3** renders this "mixed-species-pathway" unlikely. Considering that aluminum carboxylate reactions with exc. $H_3B \cdot SMe_2$ lead to ill-defined product mixtures supports speculations that a non-aluminum-containing compound promotes CO_2 reduction and it is likely to include the tetrahydroborate anion as a potent hydride transfer group.

Very recently, we had reported a cationic aluminum dihydride complex bearing a bis(NHI) ligand with mesityl substituents at the imidazoline nitrogen atoms of the ligand.[14a] In the light of our study of **4** and 7^+ we conceived that the bulkier bis(NHI) aluminum dihydride 9^+ (with Dip instead of mesityl groups, Dip = 2,6-diisopropylphenyl) would be a suitable target to provide insight into (i) the difference between complexes with one Al center (9^+) and two Al centers (**1**), and (ii) the difference between cationic and uncharged aluminum dihydrides with regard to catalytic activity for CO_2 reduction. Compound $9^+[OTs]^-$ readily forms upon conversion of the bis(iminiumtosylate) $8 \cdot (HOTs)_2$ with lithium aluminum hydride as concluded from ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and verified by SCXRD study and elemental analysis (Scheme 2, see the SI Figure S40, Ts = tosyl = p-tolylsulfonyl). We tested the suitability of $9^+[OTs]^-$ as a (pre)catalyst for CO_2 reduction (i.e. hydroboration) with $H_3B \cdot SMe_2$ and it exhibited substantially lower activity as **1a** (Table 1, Entries 3 and 1). Presumably, the decreased activity of 9^+ is connected to the lower hydride-donor character of the cationic system as compared to uncharged **1**

We had previously described the bis(NHI) substituted boron dihydride salt $10^+[OTs]^-$ (Scheme 3).[14d] It was in order to include this compound in this study due to its obvious structural resemblance to $9^+[OTs]^-$ and because of our ongoing interest in comparing the reactivities of borohydrides and aluminum hydrides. The reaction of $10^+[OTs]^-$ in $CDCl_3$ with CO_2 (1.0–1.1 bar) furnished the borocarboxylate $11^+[OTs]^-$ within 12 h (Scheme 3). Thus, the reactivity of the boron dihydride is reminiscent to the one of the aluminum hydrides **1a,b** and the
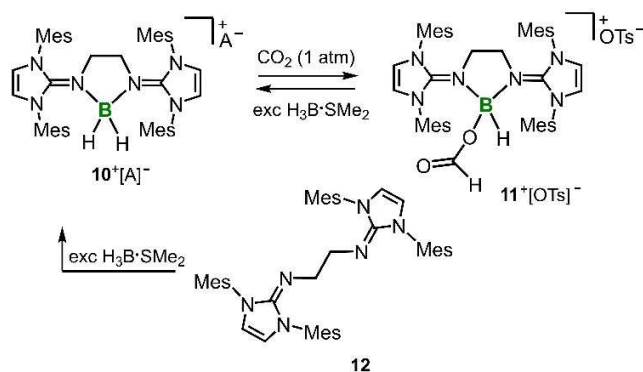
Scheme 3. Synthesis of the boron formate 11^+ and its retransformation to the boron dihydride 10^+. The bis(NHI) **12** and its conversion to 10^+ (Mes = mesityl, Ts = tosyl, NHI = N-heterocyclic imine, A = OTs (top path) or BH_4 (bottom path)).

compound might be of use for catalytic CO_2 hydroboration, as well (*vide infra*). The introduction of the carboxylate group at boron is indicated by the rise of a singlet at 5.51 ppm in the proton NMR spectrum ($CDCl_3$) that integrates to 1H. A signal at -1 ppm (J_{BH} not resolved) in the ^{11}B NMR analysis is shifted to lower field with regard to the one of the precursor (-9 ppm, CD_3CN) and suggests that the boron nucleus remains four-coordinate but has one hydride replaced by a more electron-withdrawing ligand. Moreover, the structural formulation is established by SCXRD analysis (see the SI, Figure S41). Continued exposition of $11^+[OTs]^-$ in $CDCl_3$ to CO_2 did not result in further transformation (i.e. to the borodicarboxylate) over 24 h which might reflect the generally weaker hydride donor character with respect to the one of aluminum hydrides (**1**).

Catalytic reduction of CO_2 with $H_3B\cdot SMe_2$ and use of the boron dihydride salt $10^+[OTs]^-$ as a catalyst resulted in a conversion rate similar to the one of aluminum hydride **1a** (Table 1, Entries 1 and 4). In order to gain further insight into the mechanism of CO_2 reduction using 10^+ we reacted 11^+ $[OTs]^-$ with an excess of $H_3B\cdot SMe_2$ (7 equiv) in $CDCl_3$. It occurred that in the

^1H NMR spectrum a clean transformation to 10^+ was indicated. In addition, a singlet at 3.65 ppm appeared which suggests the formation of a methoxy group. The ^{11}B NMR spectrum shows a broad resonance at -8 ppm assigned to 10^+ (J_{BH} not resolved) and a signal at 19 ppm which hints towards the formation of a trialkoxy boron species. This well-defined conversion of 11^+ to 10^+ with excess $H_3B\cdot SMe_2$ is in sharp contrast to the respective reactions of the aluminum formates **4** and **6**. It reveals that 10^+ can be transformed by CO_2 and replenished by the reductant (i.e. $H_3B\cdot SMe_2$).

The proposed mechanism for the catalytic CO_2 reduction with 10^+ is outlined in Scheme 4. The boron dihydride is transformed to the boron formate 11^+ via CO_2 insertion into the B–H bond. With concomitant release of boron formate the catalyst (10^+) is reformed via metathesis reaction between hydridoborane (i.e. reducing agent) and 11^+ (Path A). Alternately, the carbonyl group in 11^+ can be hydroborated by the reducing agent to produce Int^1 which liberates boronic acetal upon reaction with hydridoborane (Path B).
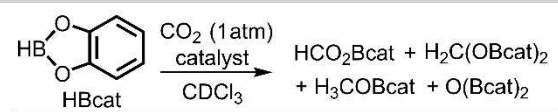
In 2018 we had published a study on the auto-ionization of the "free" bis(NHI) ligand **12** with $H_3B\cdot SMe_2$ (2 equiv) to 10^+ $[BH_4]^-$ (Scheme 3).[14a] In fact this transformation resembles the process when solubilized 1,8-bis(dimethylamino)naphthalene is brought into contact with $H_3B\cdot SMe_2$ as reported by Fontaine and coworkers.[5d] The authors verified that this bis(amino) compound, which may be classified as an organic superbase, can be used for catalytic reduction of CO_2 by $H_3B\cdot SMe_2$. Thus, it does not come as a surprise that we found the applicability of **12** for the very same purpose. Within 3 hours a solution (1 molar) of $H_3B\cdot SMe_2$ in $CDCl_3$ containing 5 mol% (i.e. $^5/_3$ mol% referred to active B–H functionalities) of **12** is near-quantitatively converted to alkoxyborane equivalents at 1.0–1.1 bar CO_2 pressure (Table 1, Entry 5). The conversion rate exceeds the one observed for the use of aluminum hydride **1b** (Table 1, Entry 2). Interestingly, the catalytic cycle suggested by Fontaine and coworkers for the use of the bis(amino)naphthalene comprises
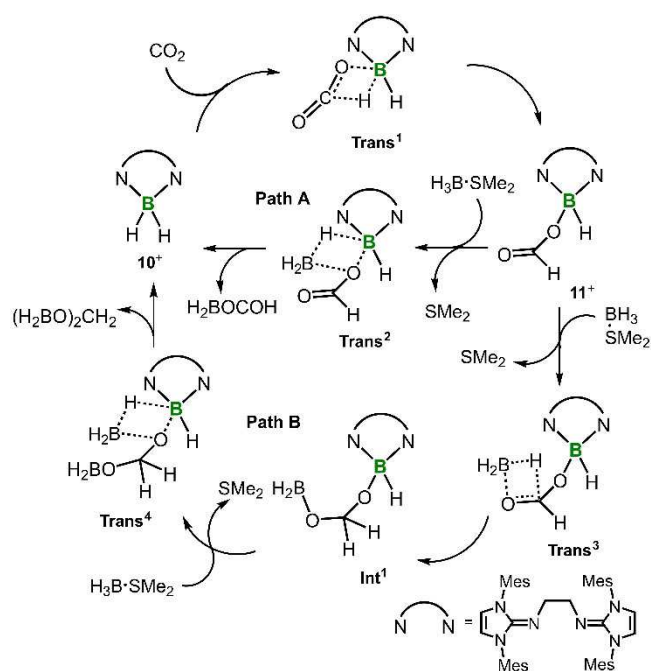
Scheme 4. Suggested catalytic cycle for the reduction of CO_2 with $H_3B\cdot SMe_2$ using $10^+[OTs]^-$ as a catalyst. Cationic charge omitted for clarity. A reminiscent mechanism might apply to the use of catecholborane as hydride source.

the formation of a boronium dihydride species of type 10^+ but no boron carboxylate species of type 11^+ is suggested. This observation raises the question if the action of $10^+[OTs]^-$ as a catalyst relies on the intermediate formation of boron formate 11^+ or on ligand detachment and the provision of **12** as the active species. Given that the conversion rate for the use of 10^+ $[OTs]^-$ significantly differs from the one for the use of **12** we consider a boron-centered mechanism as outlined in Scheme 4 viable (for $10^+[OTs]^-$) that differs from the mechanism for the use of a bidentate organic superbase (e.g. 1,8-bis(dimethylamino)naphthalene, **12**) as proposed by Fontaine.[5d] Taking into account that **12** can form 10^+ when reacted with $H_3B\cdot SMe_2$ we assume that its activity as a (pre)catalyst might rely on a dual mechanism running in part via 11^+ (Scheme 4) and in part following the catalytic cycle of Fontaine which does not involve the formation of an analoguous bis(amino) boron formate.[5d]

As **12** had turned out to exhibit the highest catalytic activity we also used it in combination with catecholborane (HBcat) and 9-BBN–H (9-borabicyclo[3.3.1]nonane, HBBN) as alternate reductants. These boranes are commonly acknowledged to be less potent hydroboration agents than $H_3B\cdot SMe_2$. Still, when using **12** as a (pre)catalyst we observed near-quantitative conversion of either borane within 13 h when exposed to a CO_2 atmosphere (1.0–1.1 bar) in $CDCl_3$. In case of HBcat ^1H and ^{11}B NMR analysis confirmed the formation of $H_3COBcat$ and $O(Bcat)_2$ (presumably along with $H_2C(OBcat)_2$ and HCO_2Bcat, see the SI). When the dialkylborane is used the NMR analysis suggested the formation of a mixture of H_3COBBN, $O(BBN)_2$, $H_2C(OBBN)_2$, and $HCOO(BBN)$ similar to the report of Cantat and coworkers on

Table 2. Results on catalytic hydroboration/reduction of CO_2 with catecholborane using NHI-based catalysts.

Entry	cat. (mol%)	Time	consumed$_{HBcat}$	yield$_{MeOBcat}$
1	**4** (3%)	4 h	53%	13%
		15 h	73%	17%
		21 h	75%	17%
2	**9$^+$[OTs]$^-$** (3%)	4 h	23%	traces
		24 h	35%	2%
3	**10$^+$[OTs]$^-$** (3%)	14 h	87%	n.a.
		≤22 h	99+%	n.a.
4	**11$^+$[OTs]$^-$** (3%)	4 h	45%	9%
		15 h	88%	23%
		≤22 h	99+%	n.a.
5	**12** (4%)	13 h	92%	n.a.
		≤17 h	99+%	n.a.

Remarks: Solutions (ca. 1 molar) of catecholborane in $CDCl_3$ with catalyst (3 or 4 mol%) exposed to CO_2 (1.0-1.1 bar) at room temperature (20-25 °C). NMR samples drawn under CO_2 atm. at indicated reaction time. NMR samples filled under N_2 atm. (no degassing). Data recorded approx. 30 min after filling. Consumption of HBcat estimated from relative intensities in ^{11}B NMR. Yield of MeOBcat determined by relative intensities (^{1}H NMR) of MeOBcat signal to signal of naphthalene standard.

the analogous conversion using various organic nitrogen bases as catalysts (see the SI, Figures S37, S38).[17] Given that **12** promotes the CO_2 reduction with HBcat we also probed selected boron and aluminum complexes as catalysts for comparison. The results are outlined in Table 2. In accordance with the decreased hydroboration activity of HBcat in comparison to $H_3B \cdot SMe_2$ the conversions generally take longer and a lower ratio of methoxy containing products is obtained. Unsurprisingly, the relative catalytic activity of the compounds follows the trend from the trihydridoborane reactions (Table 1) with **12** being the most potent catalyst and **9$^+$** showing the by far lowest conversion rates. This suggests that a similar mechanism for the CO_2 hydroboration is at work for either reducing agent.

In summary, we have demonstrated the applicability of various aluminum and boron hydride complexes **1a,b**, **9$^+$**, **10$^+$**, **11$^+$**, as well as the organic superbase **12** for the catalytic reduction of CO_2 with $H_3B \cdot SMe_2$, catecholborane, and 9-BBN–H as a hydride source. In this regard, the "free" bis(NHI) ligand **12** was found to be the most active (pre)catalyst. The bulkier aluminum hydride **1b** exhibited comparable conversion rates while the less congested aluminum hydride **1a** was significantly less active. The bis(NHI) aluminum dihydride salt **9$^+$**[OTs]$^-$ possessed lower activity than **1a**. The boron dihydride salt **10$^+$** [OTs]$^-$ proved to be a far more potent catalyst than its cationic aluminum congener (**9$^+$**). The metal(loid) hydrides (**1**, **10$^+$**) were demonstrated to form metal formate complexes (**4–7$^+$**, **11$^+$**) upon conversion with CO_2. The tetracarboxylate **6**, the dicarboxylate **4**, and the monocarboxylates **7$^+$**[$HCO_2(B(C_6F_5)_3)_2$]$^-$, as well

as **11$^+$**[OTs]$^-$ were isolated at room temperature under an atmosphere of argon or nitrogen. The aluminum formates **4** and **6** were shown to form ill-defined product mixtures upon reaction with an excess $H_3B \cdot SMe_2$. From the boron formate **11$^+$** the dihydride **10$^+$** was replenished by reaction with $H_3B \cdot SMe_2$. For **1a,b** it is hypothesized that an aluminum formate is initially formed which converts with the borane to a complex product mixture that contains the actual catalytically active species. For **10$^+$** the relevant processes (e.g. CO_2 insertion, σ-bond metathesis) are supposed to majorly occur at the bis(NHI)-bonded boron center. For **12** the [BH_4]$^-$ anion formed via autoionization between bis(NHI) and $H_3B \cdot SMe_2$ is believed to function as the hydride transferring species.

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Conflict of Interest

The authors declare no conflict of interest.

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