Catalytic CO₂ Reduction with Boron- and Aluminum Hydrides

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The previously reported dimeric NHI aluminum dihydrides 1a,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 (CO₂) 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 1a exhibited lower catalytic activity than the bulkier 1b. 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 CO₂ reduction the compounds were subjected to stoichiometric reactivity studies with the borane or CO₂. 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 (1a,b, 9−, 10−, 12) follows an individual mechanistic pathway for CO₂ 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.[31] 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)s catalysis[2] and organocatalysis[5] 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 CO₂. A few years ago, the number of studies on organocatalytic CO₂ transformations, particularly with regard to hydrogenation/reduction, started to surge.[4b,5] Here, strong Brønsted/Lewis bases as N-heterocyclic carbenes (NHC, A) or triazabicyclodecenes (B, TBD) are typically implemented to promote chemical reduction of CO₂ (Figure 1). In recent times, electron-precise complexes of s- and p-block metal(loid)s have made a similar upcoming for catalytic CO₂ 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). The successful implementation of this type of compounds for the catalytic

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 CO₂ binding that are both based on N-heterocyclic imine (NHI). Mes = mesityl, Dip = 2,6-disisopropylphenyl, icosahedron = CH₆₋₁₇Cl₁₅.
reduction of CO2 has, however, not been described. In 2018, the group of Aldridge outlined the reactivity of 1,3-diketiminato aluminum hydride (E) and selected derivatives with CO2, catecholborane and borane dimethylsulfide complex (Figure 1).[10] The authors did not detail the use of their aluminum hydrides for a catalytically driven CO2 reduction. Notably, reactivity studies on a very similar but less sterically congested aluminum hydride with CO2 were presented very recently but also no catalytic process was described.[11] In the context of CO2 transformations with aluminum complexes a study of Myers and Berben on catalytic dehydrogenation of formic acid to CO2 and H2 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 CO2. These compounds have been part of previous studies.[13,14] Notably, organic superbases containing the NHI group have been described to reversibly bond to CO2 (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). Accordingly, we exposed a solution of pinacolborane in CDC13 to an atmosphere of CO2 (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 1 b as a (pre)catalyst to 60 °C for several hours just traces of desired methoxyborane were detected via 11B NMR analysis. This agrees with the generally lower susceptibility of CO2 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 CO2 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 1 b (Table 1, Entries 1 and 2). With regard to mechanistic investigations one must note that the reaction of 1 b with H2B·SMe2 (4 equivalents) had been reported to yield the aluminum borohydride 3 (Scheme 1).[14] In CDC13 solution 3 does not convert when exposed to an atmosphere of CO2 which indicates that initial reaction between 1 b and the borane is not a viable pathway for the concerned catalytic reduction. In contrast, a solution of 1 b in CDC13 quantitatively reacts with CO2 (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 (CDCl3) with 2H relative intensity. Also, we obtained a single crystal of 4 that was determined to the diurate 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 1 a in CDCl3, to CO2 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 CDCl3 transforms into a tetracarboxylate species when kept in a CO2 atmosphere for an additional period of 8 days (Scheme 1). This reduced susceptibility of the “second” hydride at the aluminum center for CO2 insertion is in agreement with the finding that CDCl3 solutions of the bistriphens 2 a and 2 b do not react with CO2 on a 1 to 5 days timescale.

Table 1. Results on catalytic hydroboration/reduction of CO2 with borane dimethylsulfide complex using NHI-based catalysts.

| Entry | cat. (mol%) | Time | Yield |
|-------|-------------|------|-------|
| 1     | 1 a (5%)    | 1 h  | 72%   |
| 2     | 1 b (5%)    | 1 h  | 63%   |
| 3     | 9[b]OTs–   | 1 h  | 6%    |
| 4     | 10[b]OTs–  | 1 h  | 28%   |
| 5     | 12 (9%)    | 1 h  | 90%   |

Remarks: Solutions (ca. 1 mol) of H2B·SMe2 in CDCl3 with (pre)catalyst (5 or 4 mol%) was normalized to active hydride in CO2 atmosphere (1.0–1.1 bar) at room temperature (20–25 °C). NMR samples drawn under CO2 atm. indicated reaction time and filled under N2 atm. (no degassing). Data recorded approx. 30 min after filling. Yield of “MeO” determined by relative intensities (1H NMR) of alkyne to SMe2 signals.
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 aluminum carboxylate 4. The reactions with the strong Lewis acids Ph$_3$C$^+$ (cationic, used as Ph$_3$C$^+[Al(OR)_4]$) and B(C$_6$F$_5$)$_3$ (uncharged) in CDCl$_3$ solution were probed in an NMR sample tube (Scheme 2, RF = 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$_6$F$_5$)$_3$ 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$_6$F$_5$)$_3$)$_2$]$^-$ anion, respectively, is concluded from $^1$H NMR data.

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 = 1.785(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), N1–Al1–N4 = 93.4(1), O1–C28–O2 = 128.8(1); Al–Al = 2.746(1).

Scheme 2. Syntheses of the cationic aluminum complexes 7$^+$ and 9$^+$ via formate group abstraction from 4 or dehydrogenative coupling between 8·[HOTs]$^-$ and Li$^+${[AlH$_4$]}$_n$ ($A$ = HCO$_2$(B(C$_6$F$_5$)$_3$)$_2$ or Al(OR)$_4$); $A_1$ = OTs; Dip = 2,6-diisopropylphenyl, Ts = tosyl, R$^F$ = C(CF$_3$)$_3$.

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), N1–Al1–N4 = 93.4(1), O1–C28–O2 = 128.8(1); Al–Al = 2.746(1).
and $^{11}$B NMR analysis. As the $^1$H NMR spectrum of $\ce{[BH4]}$ 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$_2$N$_2$ 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$_2$B·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 NH$_2$ ligand species in the $^1$H 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$_2$B·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$_2$B·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 more upfield shifted resonance can clearly be assigned to $[\ce{BH4}]^-$ 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 $[\ce{BH4}]^-$ signal was considerably increased and only traces of the two broader resonances were shown (see the SI, Figures S26, S28). The formation of $[\ce{BH4}]^-$ is of particular interest because traces of Na[Na]$^-$ had been reported to catalyze the reduction of CO$_2$ to trimethoxyboroxine with H$_2$B·thf in THF.

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$_2$B·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$_2$B·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 imidazolidine nitrogen atoms of the ligand.$^{14d}$ 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-disopropylphenyl) 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(iminomethyl)borane (vide supra) $8$-[HOTs], with lithium aluminum hydride as concluded from $^1$H and $^{13}$C($^1$H) NMR spectroscopy and verified by SCXRD study and elemental analysis (Scheme 2, see the SI Figure S40). Ts$^-$ 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]$^-$ with in $12$ h (Scheme 3). Thus, the reactivity of the boron dihydride is reminiscent to the one of the aluminum hydrides $1a,b$ and the
compound might be of use for catalytic CO₂ 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 (CDCl₃) that integrates to 1H. A signal at −1 ppm (δₓ not resolved) in the ¹¹B NMR analysis is shifted to lower field with regard to the one of the precursor (−9 ppm, CD₂CN) 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 CDCl₃ to CO₂ 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 CO₂ with H₃B·SMe₂ and use of the boron dihydride salt ¹⁰⁻[OTs]⁻ as a catalyst resulted in a conversion rate similar to the one of aluminum hydride ¹¹a (Table 1, Entries 1 and 4). In order to gain further insight into the mechanism of CO₂ reduction using ¹⁰⁻ we reacted ¹¹⁻[OTs]⁻ with an excess of H₃B·SMe₂ (7 equiv) in CDCl₃. 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 ¹¹B NMR spectrum shows a broad resonance at −8 ppm assigned to ¹⁰⁻ (δₓ 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 H₃B·SMe₂ is in sharp contrast to the respective reactions of the aluminum formates 4 and 6. It reveals that ¹⁰⁺ can be transformed by CO₂ and replenished by the reductant (i.e. H₃B·SMe₂).

The proposed mechanism for the catalytic CO₂ reduction with ¹⁰⁻ is outlined in Scheme 4. The boron dihydride is transformed to the boron formate ¹⁰⁻ via CO₂ insertion into the B–H bond. With concomitant release of boron formate the catalyst (¹⁰⁺) is reformed via metathesis reaction between hydrodiborane (i.e. reducing agent) and ¹¹⁻ (Path A). Alternatively, the carbonyl group in ¹¹⁻ can be hydroborated by the reducing agent to produce Int² which liberates boronic acetal upon reaction with hydrodiborane (Path B).

In 2018 we had published a study on the auto-ionization of the "free" bis(NH) ligand ¹² with H₃B·SMe₂ (2 equiv) to ¹⁰⁻[BH₄]⁻ (Scheme 3).¹³ In fact this transformation resembles the process when solubilized 1,8-bis(dimethylamino)naphthalene is brought into contact with H₃B·SMe₂ as reported by Fontaine and coworkers.¹⁴ The authors verified that this bis(amino) compound, which may be classified as an organic superbase (e.g. 1,8-bis(dimethylamino)naphthalene, ¹²) as proposed by Fontaine.¹⁴ Taking into account that ¹² can form ¹⁰⁻ when reacted with H₃B·SMe₂ 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 analogous bis(amino) boron formate.¹⁵

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 hydroborating agents than H₃B·SMe₂. Still, when using ¹² as a (pre)catalyst we observed near-quantitative conversion of either borane within 13 h when exposed to a CO₂ atmosphere (1.0–1.1 bar) in CDCl₃. In case of HBCat ¹H and ¹¹B NMR analysis confirmed the formation of H₃COBcat and O(Bcat)₂ (presumably along with H₃C(OBcat)_2 and HCO₂Bcat, see the SI). When the dialkylborane is used the NMR analysis suggested the formation of a mixture of H₃COBBN, O(BBBN)₃, H₃C(OBBN)₃, and HCOO(BBN) similar to the report of Cantat and coworkers on

![Scheme 4. Suggested catalytic cycle for the reduction of CO₂ with H₃B·SMe₂ using ¹⁰⁻[OTs]⁻ as a catalyst. Cationic charge omitted for clarity. A likely reminiscent mechanism might apply to the use of catecholborane as hydride source.](image-url)
Table 2. Results on catalytic hydroboration/reduction of CO₂ with catecholborane using NH₃-based catalysts.

| Entry | cat. (mol%) | Time (min) | ηBHcat (%) | Yield H₂ΟBHcat (%) |
|-------|-------------|------------|------------|--------------------|
| 1     | 4 (3%)      | 4          | 63         | 13                 |
|       |             | 15         | 73         | 17                 |
|       |             | 21         | 75         | 17                 |
| 2     | 9 (OTs)⁻ (3%) | 4          | 23         | traces             |
|       |             | 24         | 35         | 2%                 |
| 3     | 10 (OTs)⁻ (3%) | 4          | 87         | 99%                |
|       |             | 14          | 87         | 99%                |
| 4     | 11 (OTs)⁻ (3%) | 4          | 45         | 9%                 |
|       |             | 15          | 88         | 23%                |
|       |             | 22          | 88         | 99%                |
| 5     | 12 (4%)     | 13          | 92%        | n.a.               |
|       |             | 17          | 92%        | n.a.               |

Remarks: Solutions (ca. 1 molar) of catecholborane in CDCI₃ with catalyst (3 or 4 mol%) exposed to CO₂ (1.0-1.1 bar) at room temperature (20-25 °C). NMR samples drawn under CO₂ atm. at indicated reaction time. NMR samples filled under N₂ atm. (no degassing). Data recorded approx. 30 min after filling.

Consumption of HBcat estimated from relative intensities in ¹¹B-NMR. Yield of MeOBcat determined by relative intensities (¹H-NMR) of MeOBcat signal to signal of naphthalene standard.

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 H₃B·SMEO₂. From the boron formate 11⁻ the dihydride 10⁺ was replenished by reaction with H₃B·SMEO₂. For 1 a 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. CO₂ insertion, σ-bond metathesis) are supposed to majorly occur at the bis(NH₃)-bonded boron center. For 12 the [BH₄⁻] anion formed via auto-ionization between bis(NH₃) and H₃B·SMEO₂ 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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