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Metal-free disproportionation of formic acid mediated by organoboranes†

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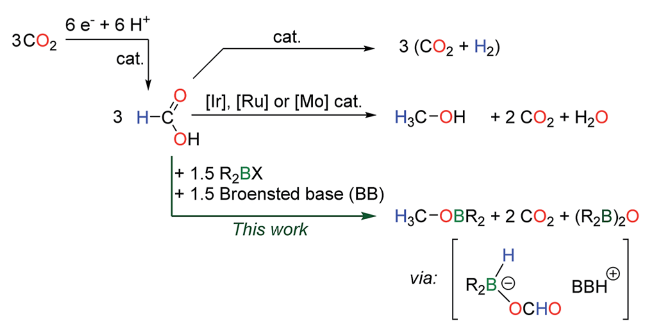
In the presence of dialkylboranes, formic acid can be converted to formaldehyde and methanol derivatives without the need for an external reductant. This reactivity, in which formates serve as the sole carbon and hydride sources, represents the first example of the disproportionation of formate anions under metal-free conditions. Capitalizing on both experimental and computational (DFT) mechanistic considerations, the role of transient borohydride is highlighted in the reduction of formates and this reactivity was further exemplified in the methylation of TMP (2,2,6,6-tetramethylpiperidine) and in the transfer hydroboration reactions for the reduction of aldehydes.

Introduction

Formic acid is an attractive reductant in organic chemistry because it is a benign and liquid surrogate for molecular hydrogen. In fact, the use of HCO_2H in transfer hydrogenation has been successfully applied to a variety of organic substrates,[1] including carbonyl groups and C=C systems, and the development of catalysts for these transformations is still under active study.[2] The reasons behind this success originate in the kinetic and thermodynamic properties of HCO_2H. Indeed, formic acid presents a redox potential similar to H_2 $E^0(CO_2/HCO_2H = -0.61$ V *vs.* $E^0(H_2O/H_2 = -0.41$ V at pH = 7 *vs.* NHE) but the C–H bond has a Bond Dissociation Energy (BDE) which is about 16 kcal mol^{-1} weaker[3] than the H–H bond and it is thus easier to activate at a metal center. More recently, the high hydrogen content of formic acid (4.4%) has been recognized as a means to store H_2 in liquid form, under ambient conditions.[4] This concept relies on the selective decomposition of HCO_2H to H_2 and CO_2 and a plethora of molecular catalysts have been designed to catalyze this important transformation.[5] While catalysts based on noble metals are the most efficient systems, the state-of-the-art is currently shifting towards earth abundant metal catalysts, based on iron[6] or aluminum complexes.[7] In 2015, our group reported the first organic catalysts for the dehydrogenation of formic acid, using dialkyboranes.[8]

Beyond formic acid, methanol can store 12.1 wt% hydrogen and this high energy chemical (4900 *vs.* 2104 W h L^{-1} for HCOOH) represents an excellent energy vector. Formic acid has been recently proposed as a sustainable intermediate in the production of methanol.[9] This strategy relies on the catalytic electroreduction of CO_2 to HCO_2H, a technically and economically viable process which is under pilot development.[10] HCO_2H can then serve as a C–H bond shuttle to yield methanol, assuming that efficient systems can promote the disproportionation of formic acid (Scheme 1). Nevertheless, the disproportionation of HCO_2H is a difficult transformation because the dehydrogenation of formic acid is favored over the reduction of a formate group. The first catalysts for the disproportionation of formic acid were only unveiled in 2013 (ref. 11) by Goldberg, Miller *et al.* who showed that iridium(III) complexes could convert formic acid to methanol with a maximum yield of 2.6%. H_2 is in fact the main product during the iridium-catalyzed decomposition of HCO_2H. In 2014, our group reported ruthenium(II) catalysts for this transformation[9] and the selective conversion of HCO_2H to 50% methanol was achieved. While the ruthenium catalysts still represent the state of the art in this transformation, Parkin *et al.* described the first catalysts without noble metals, using molybdenum(II) complexes.[12] With all these systems, H_2 is produced as a competing product in at least 50% yield.



Scheme 1 Disproportionation of formic acid to the methanol level and the competing dehydrogenation.

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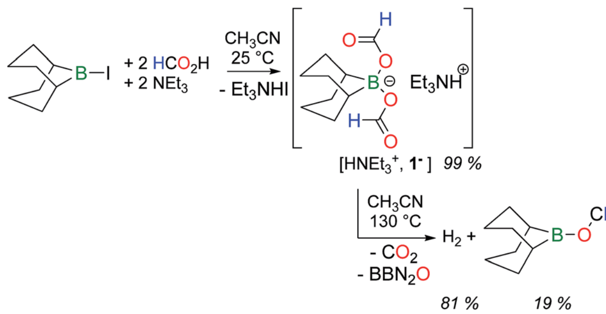
Reasoning that on the one hand dialkylboranes are catalysts for the dehydrogenation of formic acid[8] and that on the other hand hydroboranes can reduce CO_2 to methoxyboranes, in the presence of a catalytic amount of an organic base,[13] we have sought metal-free systems able to mediate the disproportionation of formic acid. Herein, we demonstrate that stoichiometric amounts of dialkyborane derivatives can convert formates to formaldehyde and methanol derivatives, for the first time. Mechanistic insights derived from the experimental results and DFT calculations highlight the role of transient borohydride in these transformations.

Results and discussion

9-Iodo-9-borabicyclo[3.3.1]nonane (BBN–I) was shown to promote the catalytic decarboxylation and dehydrogenation of formic acid and its reaction chemistry was thus explored in the presence of formate anions.[8] Adding 2 molar equivalents of formic acid and triethylamine to an acetonitrile solution of BBN–I affords bis(formoxy)borate [$HNEt_3^+$, **1**$^-$] along with $HNEt_3I$, at room temperature (RT) (eqn (1)).



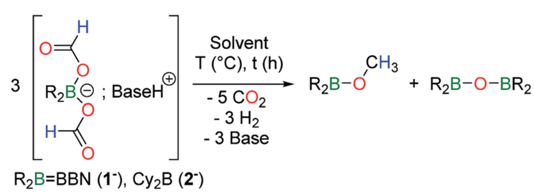
(1)

(2)

Heating this mixture at 130 °C leads to the complete decomposition of the formate ligands in **1**$^-$ and the concomitant formation of CO_2 was observed by GC and ^{13}C NMR (eqn (2)). As expected, H_2 is also observed in the gas phase. Notably, a singlet at 3.71 ppm is also observed in the ^1H NMR spectrum, coupled with a weak resonance at 53.9 ppm that was attributed to a primary carbon in the ^{13}C NMR spectrum. To verify this chemical behavior, the same chemical sequence was reproduced with $H^{13}CO_2H$. At RT, in acetonitrile, the protons of the formate in ^{13}C-labelled **1**$^-$ display a doublet ($\delta = 8.43$ ppm, $^1J_{C-H} = 202$ Hz) coupled to a singlet at 168.1 ppm in the ^{13}C NMR spectrum. After 3 h at 130 °C, the ^1H NMR spectrum of the crude mixture indicates the formation of H_2 gas and $^{13}CH_3OBBN$ (^1H NMR: $\delta = 3.71$ ppm, $^1J_{C-H} = 143$ Hz; ^{13}C NMR: $\delta = 53.9$ ppm). After 20 h, $^{13}CO_2$ and $^{13}CH_3OBBN$ were the only ^{13}C-enriched products observed in solution. After the removal of the volatiles under a reduced pressure, the resulting solid was dissolved in d_8-toluene to afford a homogeneous solution comprising methoxyborane ($\delta(^{11}B) = 57$ ppm) and diboroxane $(BBN)_2O$ ($\delta(^{11}B) = 59$ ppm) as the sole boron-containing products. These results clearly demonstrate that formate anions can disproportionate to methoxides in the coordination sphere of boron, with the associated release of CO_2 and diboroxane. The parallel formation of H_2 and CH_3OBBN shows that the disproportionation and dehydrogenation of formic acid are competing in the presence of the dialkylborane, although stoichiometric amounts of protons are present in the reaction mixture (in the form of $HNEt_3^+$) with respect to the formates. Under catalytic conditions (using 5 mol% [$HNEt_3^+$, **1**$^-$]), the dehydrogenation of HCO_2H was observed after 24 h at 130 °C, together with only a catalytic quantity of CH_3OBBN (<5 mol%).

[$HNEt_3^+$, **1**$^-$] was isolated from the reaction between 9-BBN, HCOOH and triethylamine and its disproportionation to CH_3OBBN was investigated to gain further insights into this novel transformation. The thermolysis of [$HNEt_3^+$, **1**$^-$] is inefficient in THF or benzene and it is best carried out in acetonitrile at 130 °C (entries 1–4 in Table 1). Under these conditions, [$HNEt_3^+$, **1**$^-$], is completely decomposed to H_2 and CH_3OBBN after 10.5 h (entry 4 in Table 1). CH_3OBBN is formed in 39% yield, meaning that 39% of the C–H bonds present in the formate ligands of **1**$^-$ are efficiently preserved as C–H bonds in the methoxide ligand (see ESI†). Increasing the reaction temperature to 150 °C only affects the rate of the thermolysis and CH_3OBBN is obtained in 33% yield after only 4 h. Importantly, the disproportionation of formates is not specific to the BBN framework and the dicyclohexylborane derivative [$HNEt_3^+$, **2**$^-$] is also prone to generate the corresponding Cy_2BOCH_3. Although the latter gave low yields of the methoxyborane at 130 °C, presumably due to the thermal instability of the reaction intermediates, the reaction proceeded smoothly at 120 °C to afford Cy_2BOCH_3 in 38% yield after 7 h (entry 7 in Table 1). In all cases, free methanol can be ultimately generated by hydrolysis of methoxyborane (see ESI†). The nature of the base used to prepare the starting bis(formoxy)borate also influences the efficiency of the disproportionation. Indeed, the thermolysis of [iPr_2EtNH^+, **1**$^-$] at 130 °C leads to CH_3OBBN in 50% yield within only 4.5 h. This improved selectivity demonstrates the positive influence of bulky tertiary amines, such as iPr_2EtN, which might arise from the decreased affinity of the amine for the boron center.[14]

Table 1 Boron mediated disproportionation of formate anions into methoxyboranes[a]



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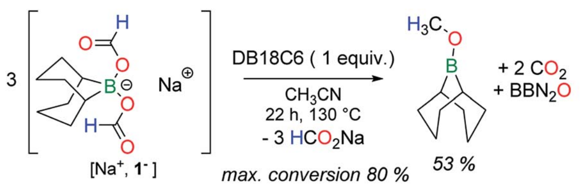
Entry	R_2B	$BaseH^+$	t[c] [h]	T [°C]	Solvent	Yield[b] [%]
1	BBN	Et_3NH^+	>48 h	130	d_8-THF	<5
2	BBN	Et_3NH^+	>48 h	130	C_6D_6	<5
3	BBN	Et_3NH^+	4	150	CD_3CN	33
4	BBN	Et_3NH^+	10.5	130	CD_3CN	39
5	BBN	iPr_2EtNH^+	4.5	130	CD_3CN	50
6	BCy_2	Et_3NH^+	2.5	130	CD_3CN	<5
7	BCy_2	Et_3NH^+	7	120	CD_3CN	38

[a] Reaction conditions: 0.125 mmol **1**$^-$ or **2**$^-$, 0.4 mL solvent. [b] Yields determined by ^1H NMR using mesitylene (10 μL); mean value over at least 2 runs. [c] Time required to obtain >95% conversion of formate.

To assess whether H_2, released by dehydrogenation, plays any role in disproportionation, the corresponding bis(formoxy) borate [Et_3ND^+, $R_2B(OCHO)_2^-$] was synthesized *in situ* in toluene at RT from HCO_2D. As expected, its thermolysis at 130 °C in CH_3CN affords gaseous HD ($\delta_H = 4.54$ ppm, t, $^1J_{HD} = 43$ Hz), as made evident by ^1H NMR. However, no deuterium-containing reduced product (other than HD) was detected by either ^1H or ^{13}C NMR (Fig. S17†) spectroscopy at intermediate or full conversion of the formate. In addition, the thermolysis of aprotic [Na^+, $\mathbf{1}^-$] in the presence of the crown ether DB18C6 (dibenzo-18-crown-6) also affords CH_3OBBN in a 53% yield after 22 h at 130 °C (eqn (4)), thus proving that the disproportionation can proceed without dehydrogenation. In that case, the conversion reached a plateau at *ca.* 80%, induced by the release of somewhat unreactive HCO_2Na under the applied reaction conditions.



(4)

Overall, the disproportionation of formate anions mediated by dialkylboranes proceeds with yields and selectivities (up to 53%), comparable to state-of-the-art metal catalysts.[9,11,12]

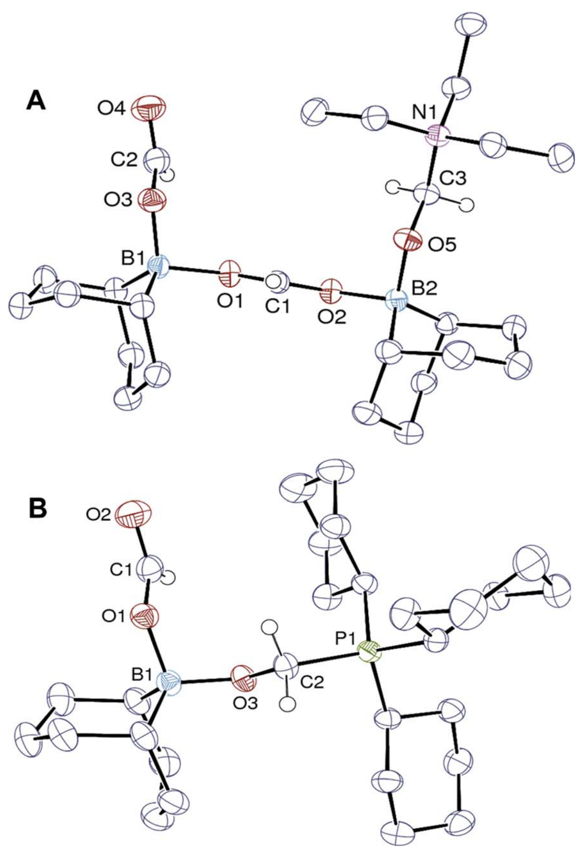
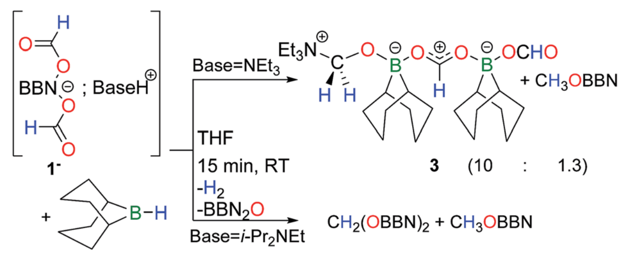


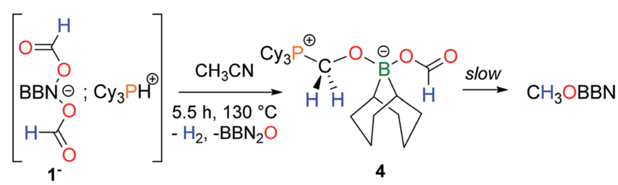
Fig. 1 ORTEP views of **3** (A) and **4** (B). The hydrogen atoms of the BBN, ethyl and cyclohexyl groups are omitted for clarity.

Although stoichiometric amounts of dialkylboranes are required to promote the disproportionation of formates, the formation of methoxyboranes from $\mathbf{1}^-$ and $\mathbf{2}^-$ represents the first examples of metal-free mediated disproportionations of formates. The mechanism of this transformation was thus investigated both experimentally and computationally in order to track possible reaction intermediates. Monitoring the thermal decomposition of [$HNEt_3^+$, $\mathbf{1}^-$] by NMR reveals the formation of a single transient species **3** (<5% yield), characterized by a singlet at 4.40 ppm in the ^1H NMR spectrum, which is associated with a ^{13}C resonance at 80.5 ppm. Reasoning that **3** is an acetal compound, its independent synthesis was carried out by reacting hydroborane 9-BBN with [$HNEt_3^+$, $\mathbf{1}^-$] (eqn (5)). **3** is obtained as the major reduced product, along with CH_3OBBN (10 : 1.3 ratio), and the formulation of an acetal compound was confirmed by X-ray diffraction (Fig. 1A). **3** is a zwitterionic adduct of formaldehyde in which the carbon atom is bound to NEt_3 and the oxygen atom coordinates a formoxyborane group, namely BBNOCHO. The latter formate ligand coordinates a second equivalent of the Lewis acid BBNOCHO.[15]



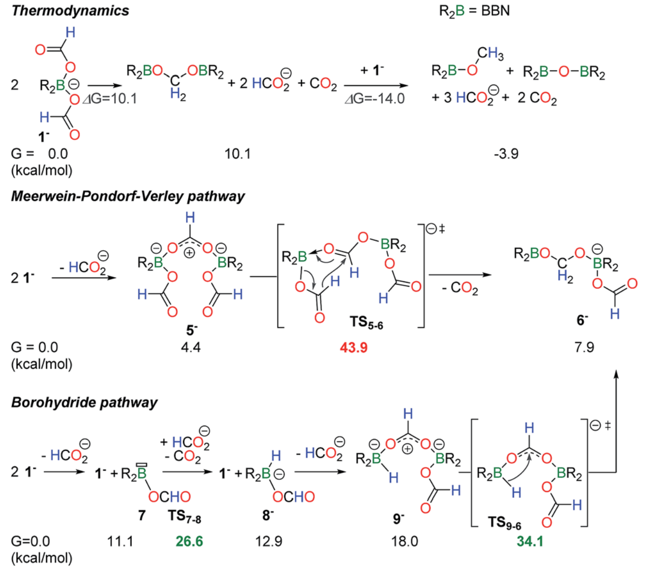
(5)

The finding that nucleophilic bases such as NEt_3 can stabilize an intermediate formaldehyde adduct suggests the occurrence of a novel and unique transformation, namely the selective disproportionation of formates to CO_2 and formaldehyde. We have thus sought a Lewis base able to direct the selectivity towards the formation of formaldehyde surrogates from the disproportionation of boron formates. A phosphonium salt [Cy_3PH^+, $\mathbf{1}^-$] was synthesized and its thermolysis leads, after 5.5 h at 130 °C, to the formation of H_2, CO_2, free PCy_3 and the formaldehyde adduct **4** as the only reduction product (eqn (6)).



(6)

The X-ray analysis of crystals obtained by slowly cooling the reaction mixture reveals that **4** features a formaldehyde unit C-coordinated to the phosphorus Lewis base and O-coordinated to a BBN–OCHO unit (Fig. 1B). It thus resembles the related (tBu$_3$PCH$_2$O)(HC(O)O)B(C_8H_{14}) isolated by Stephan and coworkers,[16] from the hydroboration of CO_2. As expected, **4** exhibits an enhanced stability towards reduction in comparison to **3**. Its conversion to CH_3OBBN is slow and requires 10 h at 130 °C to proceed (30% yield).[17]

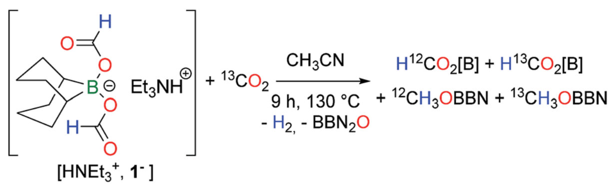


Scheme 2 Computed mechanism for the disproportionation of 1^- to the formaldehyde level. The full energy surface is provided in Scheme S1.†

The disproportionation of 1^- to $CH_2(OBBN)_2$ and CH_3OBBN was investigated using DFT calculations (M06-2X/6-311+G(d,p) level of theory, in acetonitrile (PCM)) so as to determine how a C–H bond from a formate anion can be transferred to a second formate ligand in the boron coordination sphere. The thermodynamic balance for the disproportionation of 1^- is given in Scheme 2. From 2 equiv. of 1^- the formation of $CH_2(OBBN)_2$ is slightly endergonic with $\Delta G = 10.1$ kcal mol^{-1} and 2 equiv. of HCO_2^- and 1 equiv. of CO_2 are released. Further addition of 1 equiv. of 1^- enables the formation of CH_3OBBN together with 1 equiv. of HCO_2^- and CO_2 ($\Delta G = -3.9$ kcal mol^{-1}). It is noteworthy that, under the applied reaction conditions (130 °C), 1^- also catalyzes the decarboxylation of the free HCO_2^- anions, thereby shifting the equilibria towards the formation of the products (see ESI†).

Experimental observations show that the disproportionation of 1^- to the formaldehyde redox state is rate determining, as $CH_2(OBBN)_2$ and **3** do not accumulate, and thus only the mechanism of this step was computed. Two routes can be proposed. First, transfer hydrogenation with aluminum(III) isopropoxide salts is well documented and a mechanism similar to the Meerwein–Pondorf–Verley (MPV) reaction represents a first plausible pathway.[18] In a second option, the decarboxylation of a formate ligand could afford a boron hydride, whose B–H functionality reduces a second formate anion. DFT calculations were performed to distinguish the two pathways and the results are summarized in Scheme 2, with the full energy surface being provided in Scheme S1 (ESI†). Starting from 2 equiv. of 1^-, the exclusion of one formate ligand yields dimer 5^- in a slightly endergonic process ($\Delta G = +4.4$ kcal mol^{-1}). In dimer 5^-, one formate ligand is bridging two boron centers and this activation increases the electrophilicity of the carbon atom. In fact, the NBO charge of the carbon atom in the μ^2(O,O′)–$HCOO^-$ ligand is 0.77 *vs.* 0.71 in the other two κ^1-$HCOO^-$ ligands. Hydride transfer from a monodentate formate ligand thus provides intermediate 6^-, which further dissociates into $CH_2(OBBN)_2$ and a free HCO_2^- anion. This pathway represents a boron variant of the MPV mechanism. Nevertheless, its occurrence is highly unlikely because the transition state ($\mathbf{TS_{5-6}}$) connecting 5^- and 6^- is high in energy and it involves an overall barrier of 43.9 kcal mol^{-1}, incompatible with the experimental conditions.

Alternatively, a mechanism relying on the transient formation of a borohydride species is favored. The dissociation of one formate ligand from 1^- is slightly endergonic (+11.1 kcal mol^{-1}) but it provides an unsaturated formatoborane (**7**), able to promote the decarboxylation of HCO_2^- with a low energy barrier of 15.5 kcal mol^{-1} by hydride abstraction. This process affords a reductant, BBN(H)(OCOH)$^-$ (8^-). The displacement of a formate ligand in 1^- with 8^- provides dimer 9^- (+18.0 kcal mol^{-1}) which features a bridging $HCOO^-$ ligand, similar to 5^- and **3**. Hydride transfer from boron to the bidentate formate ligand in 9^- yields 6^-, with a low energy barrier of 16.1 kcal mol^{-1}. From 6^-, the acetal $CH_2(OBBN)_2$ (+10.1 kcal mol^{-1}) can be released or trapped as adduct **3** (−8 kcal mol^{-1}) in the presence of NEt_3. Overall, this mechanism only involves an energy barrier of 34.1 kcal mol^{-1}, corresponding to the energy span between the starting materials and $\mathbf{TS_{9-6}}$, and it is compatible with thermolysis occurring within several hours at 130 °C.

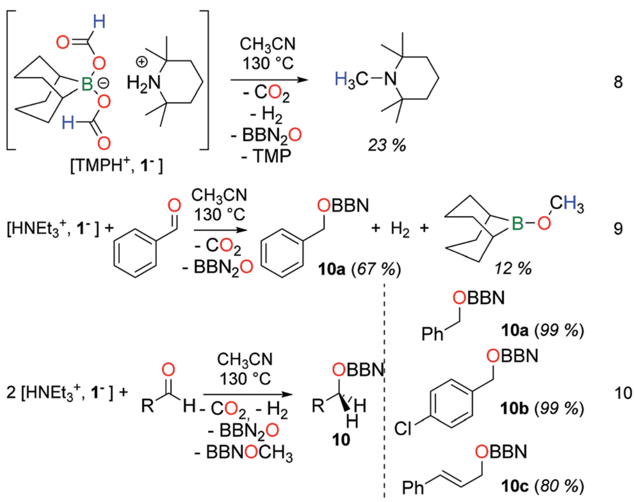


(7)

Experimentally, strong evidence for the involvement of a B–H bond was further gained by carrying out the thermolysis of [$HNEt_3^+$, $(H^{12}C(O)O)_2BBN^-$] under $^{13}CO_2$ atmosphere (1 atm) (eqn (7)). After 3 h at 130 °C, a mixture of $H^{12}C(O)O$[B] and $H^{13}C(O)O$[B] along with $^{12}CH_3OBBN$ was observed and, after 9 h, the additional formation of $^{13}CH_3OBBN$ became evident (Fig. S14†). This result stresses the presence of an equilibrium between CO_2 and $HCOO^-$ and, while such a process is unlikely for an MPV pathway, it rather points to the involvement of an intermediate borohydride species BBN(H) (OCHO)$^-$ (8^-). This proposal is also consistent with the observation that $HB(C_6F_5)_3^-$ (obtained by H_2 splitting with a Frustrated Lewis Pair) and BH_4^- are able to reduce CO_2 to the methanol and formate levels respectively.[19]

The thermal decarboxylation of a formate anion in 1^- provides a reductant (8^-) and we have computed that 8^- has a hydride donor ability similar to $BBNH_2^-$ (34 *vs.* 33 kcal mol^{-1} respectively).[20] 8^- (and 1^-) is thus a potent reductant and its reductive properties were further investigated, in the presence of various oxidants (eqn (9) and (10)). Building on the disproportionation of formates in 1^- to CH_3OBBN, the methylation of a secondary amine was attempted. The tetramethylpiperidinium salt [$TMPH^+$, 1^-] was first prepared and decomposed quantitatively within 17 h at 130 °C in acetonitrile. Interestingly, CH_3OBBN does not form under these conditions and *N*-methyl-tetramethylpiperidine was obtained instead in 23% yield, along with H_2, CO_2, BBN_2O and free TMP (eqn (8)). In this reaction, the formate ligands in 1^- serve both as a H and C source for the formation of the N–CH_3 linkage.[21]

Interestingly, when the thermolysis of $[HNEt_3^+, 1^-]$ is carried out in the presence of 1 molar equiv. of benzaldehyde, $PhCH_2OBBN$ (**10a**) is obtained in a 67% yield, further confirming that bis(formoxy)borate 1^- is able to deliver a useful reducing agent (eqn (9)). The parallel formation of CH_3OBBN (12% yield) shows that the disproportionation of formates is a surprisingly facile process from 1^-. This result represents the first example of reduction of a carbonyl substrate by transfer hydrogenation from formic acid, under metal-free conditions. It can also be described as a transfer hydroboration.[22] In fact, the reduction of various aldehydes can be efficiently carried out with 2 molar equivalents of $[HNEt_3^+, 1^-]$. Under these conditions, benzaldehyde is reduced to **10a** in 99% yield and borylethers **10b** and **10c** were obtained respectively in 99 and 80% yield from the corresponding aldehydes (eqn (10)).



Conclusions

In conclusion, we have shown that formic acid can undergo disproportionation reactions, using stoichiometric quantities of dialkylborane reagents. In the coordination sphere of boron, formate ligands were decarboxylated to provide borohydride intermediates, which were successfully utilized to promote the disproportionation of formates to formaldehyde and methanol scaffolds and the reduction of aldehydes under metal-free conditions, for the first time. Current work in our laboratory is devoted to facilitating the generation of borohydrides from formic acid and increasing the hydride donor ability of the resulting B–H group.

Acknowledgements

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