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# A Viewpoint on Chemical Reductions of Carbon–Oxygen Bonds in Renewable Feedstocks Including CO<sub>2</sub> and Biomass

*Clément Chauvier, Thibault Cantat\**

NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette, France

Carbon dioxide, Reduction, Hydrogen, Hydroboranes, Hydrosilanes, Formic Acid, Hantzsch esters

## Introduction

Over several billions of years, the anaerobic digestion of carbohydrates, produced by ancient photosynthetic organisms, has led to the accumulation of reduced and deoxygenated carbon feedstocks in the subsoil. The exploitation of these energetic fossil resources, namely oil, gas and coal, maintains the expansion of humanity by meeting its demand in energy and in raw materials. Nevertheless, the increasing scarcity of fossil resources paired with the rise of the human population calls for the use of renewable energy sources and carbon feedstocks for the development of fuels and chemicals with a low carbon footprint. Possible ways to meet these requirements involve the utilization of CO<sub>2</sub> or biomass wastes, as cheap, non-toxic, cost efficient and abundant raw materials.<sup>1</sup> Yet, their conversion into useful value-added products, currently produced through petrochemistry, requires a significant input of energy to overcome their oxidized nature and high thermodynamic stability. While the development of petrochemistry has relied on the design of efficient oxidation methods able to functionalize hydrocarbons, a smaller number of applications have emerged that involve a chemical reduction. Within the realm of fossil technologies, the choice of the electron or hydride donor, *i.e.* the reductant, is mostly

driven by its cost, reactivity and ease of handling. As such, dihydrogen is successfully utilized at the megaton scale for the upgrading of fossil fuels or as a component of syngas in the Fischer-Tropsch and oxo processes.<sup>2</sup> In contrast, aluminum and boron hydrides are preferred for the reduction of fine chemicals on small to medium industrial scales, due to their high reactivity.<sup>3</sup> We contend that energetic as well as recyclability considerations shall equally provide guidance in the design of reduction strategies and, in this viewpoint, we discuss how current reduction methods and reductants, able to cleave  $\sigma$  and  $\pi$  C–O bonds by hydride transfer, can be utilized for the conversion of organic compounds deriving from CO<sub>2</sub>, biomass or waste plastics. (The reader is referred to recent literature surveys for the direct reduction of C–O and C=O bonds by electrolysis.)<sup>4</sup> The successes, pitfalls and challenges in the field are considered within the framework of sustainable chemistry.

## 1. Specifications for a sustainable hydride donor

Arguably, main-group elements hydrides such as NaBH<sub>4</sub>, LiAlH<sub>4</sub> or sodium bis(2-methoxyethoxy)aluminumhydride (Red-Al<sup>®</sup>) are the most versatile reagents in reduction chemistry.<sup>5</sup> These compounds are indeed readily available from commercial sources and able to reduce a wide range of carbonyls, epoxides, amides, esters and carboxylic acids. Pioneering examples of CO<sub>2</sub> reduction with both LiAlH<sub>4</sub> and NaBH<sub>4</sub> were reported from 1948.<sup>6</sup> A variety of reduction products were observed and/or isolated depending on the CO<sub>2</sub>/hydride donor ratio and the temperature range, including formate (HCOO), acetal (OCH<sub>2</sub>O) and methoxide ligands (CH<sub>3</sub>O). In 2015, Cummins et al. revisited the reduction of CO<sub>2</sub> and NaBH<sub>4</sub> and isolated Na[HB(OCHO)<sub>3</sub>] as the main reduction product, under 300 psi CO<sub>2</sub>.<sup>7</sup> Importantly, the reactions proceed at room temperature without the need for a catalyst, thereby illustrating the high

reactivity of aluminum and boron hydrides towards both C=O and C–O bonds. Nonetheless, this kinetic advantage comes at an energy price.

From a thermodynamic standpoint, the formation of C–H bonds by reduction of CO<sub>2</sub> only necessitates a low energy input and the redox potential of CO<sub>2</sub> couples involving forming acid, CO, oxalic acid, methanol or methane all lie within a range of 0.17 to –0.47 V vs. NHE (25 °C; pH=0) (Scheme 1).<sup>8</sup> In contrast, the oxidation potential of LiAlH<sub>4</sub> is quite negative, with  $E^0(\text{Al}^{3+}/\text{AlH}_4^-) = -1.78 \text{ V}$  (vs. NHE).<sup>9</sup> In other words, the reduction of CO<sub>2</sub> with LiAlH<sub>4</sub> proceeds with an overpotential of ca. 1.3 V, where a 100 mV difference in potentials would suffice to ensure a quantitative reaction. The oxidation potential of NaBH<sub>4</sub> is better aligned with the potentials of CO<sub>2</sub> couples ( $E^0_{(\text{B}(\text{OH})_4^-/\text{BH}_4^-)} = -1.24 \text{ V}$  at pH = 14 and  $E^0_{(\text{B}(\text{OH})_3/\text{BH}_4^-)} = -0.48 \text{ V}$  at pH = 0 vs. NHE).<sup>9</sup> Yet, NaBH<sub>4</sub> is currently produced by the Brown–Schlesinger<sup>10</sup> or Bayer<sup>11</sup> processes, which rely on the energy-demanding electrolysis of NaCl, applying large overpotentials to obtain metallic sodium ( $E^0_{(\text{Na}^+/\text{Na})} = -2.71 \text{ V}$  vs. NHE) (Eq. 1). The latter is then reacted with hydrogen gas at high temperature (250–300 °C) to afford sodium hydride (Eq. 2), which is subsequently converted into NaBH<sub>4</sub> with trimethylborate (Eq. 3). Because an excess of sodium with respect to boron is required, the energy cost for electrolysis significantly outweighs the energy provided from NaBH<sub>4</sub> as a reductant.

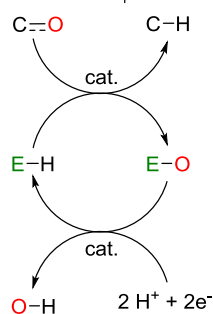


An additional drawback limits the utilization of LiAlH<sub>4</sub> or NaBH<sub>4</sub> in the large scale conversion of CO<sub>2</sub> or other renewable feedstocks: the reduction of oxygenated substrates with these hydride donors affords, after a common step of hydrolysis, stoichiometric amount of oxidized boron and

aluminum salts, which are only recyclable to hydrides at the expense of high energy costs (e.g. *via* Eq. 3).

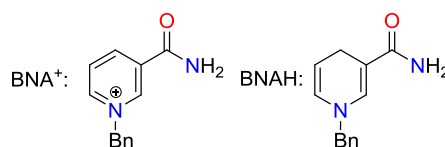
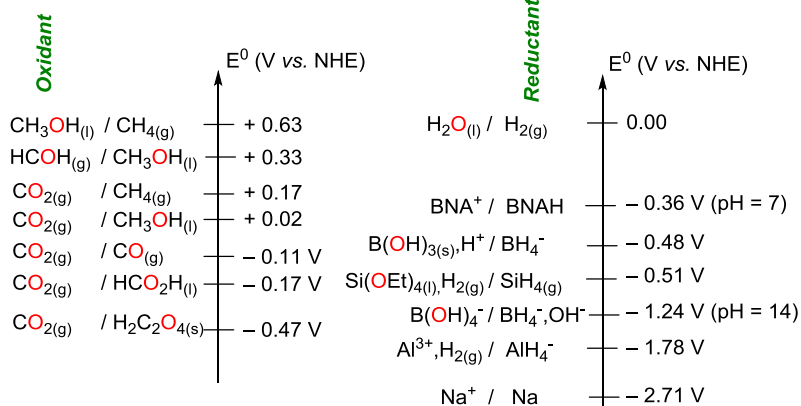
Lessons learned from main group element hydrides allow us to better define the specifications of an ideal reductant for the reduction of C=O and C–O bonds in renewable carbon feedstocks or derivatives thereof, namely carboxylic acid derivatives or carbonyls (Scheme 1). (i) From a *thermodynamic* perspective, a hydride donor (labelled E–H) should present a redox potential only slightly more negative than the redox potential of typical C–O and C=O bonds. In the following, we propose to select hydride donors with  $E^\circ(\text{E–O}/\text{E–H}) > -0.5 \text{ V vs NHE}$ . (ii) A polarized E–H bond is also desirable to enhance the rates of hydride transfer either directly to the organic oxidant or to the catalyst. This *kinetic* parameter can be tuned by changing the nature of the E element and/or the substituents on E. A more electropositive atom increases the hydridic character of the E–H bond and, at the same time, improves the affinity of E towards oxygen. (iii) Finally, methods for the *recycling* of the oxidized E–O side products to the original E–H starting materials must be readily available, with a low overpotential, to ensure the atom economy and energy efficiency of the whole process, as depicted in Scheme 1.

C-O bonds in CO<sub>2</sub>, biomass, waste plastics, etc.  
 C-O in alcohols, ethers  
 C=O in CO<sub>2</sub>, carbonyls (esters, amides, carbonates, etc.) Value-added chemicals, fuels



**Specifications:**

1. E°(E-O/E-H) is close to E°(C=O/C-H)
2. The E-H bond is polarized to facilitate H<sup>+</sup> delivery at a high rate and with enhanced selectivity
3. E-O can be recycled to E-H at a low overpotential

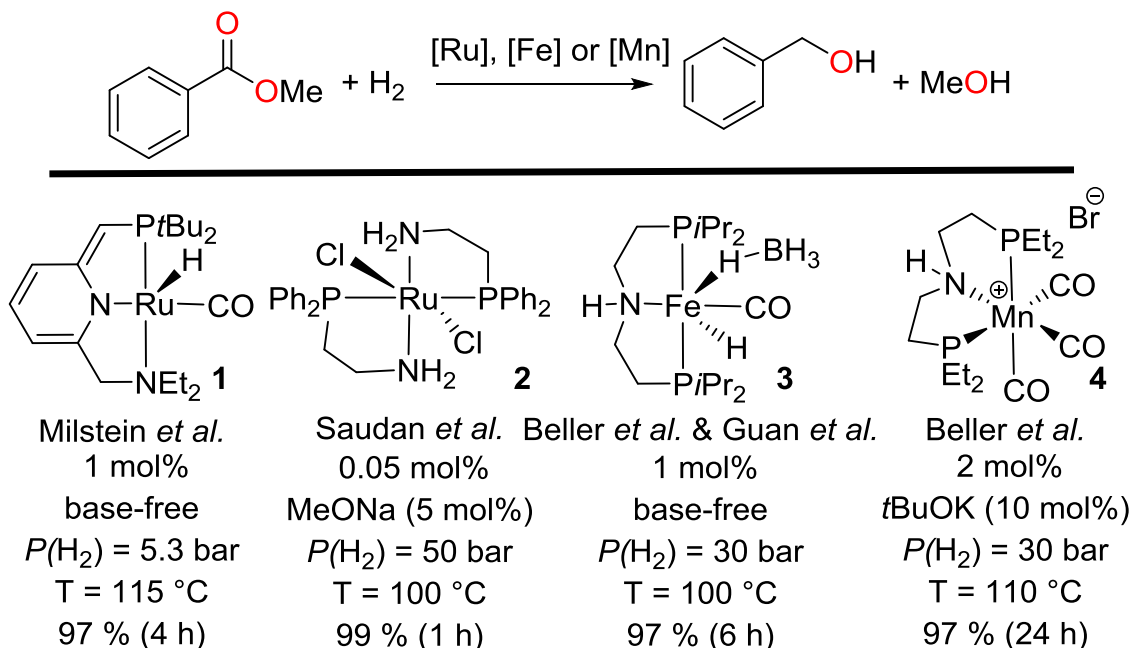


**Scheme 1. Specifications for a reductant adapted to the reduction of  $\sigma$  and  $\pi$  C-O bonds in renewable feedstocks and thermodynamic data for selected common reductants<sup>8</sup>**

## 2. Catalytic hydrogenation

Molecular hydrogen (H<sub>2</sub>) is broadly recognized as a sustainable reductant that may play a key role in the so-called *hydrogen economy* proposed by J. Bockris.<sup>12</sup> Although it is currently produced by a fossil technology, namely the steam reformation of methane, intense research efforts are being devoted to improve the cost and energy efficiencies of electro- and photo-catalytic water splitting. Chemically, H<sub>2</sub> is a non-polar gas comprising a strong  $\sigma$  bond (BDE = 104 kcal.mol<sup>-1</sup>).<sup>13</sup> For these reasons, H<sub>2</sub> is kinetically inert and catalysts are required to achieve the desired reductive transformations. Catalysis represents an outstanding opportunity to finely tune the reductive properties of H<sub>2</sub> *via* splitting of the H-H bond to generate a reduced catalytic species (e.g. a metal-hydride).<sup>14</sup> It also raises significant challenges, as finding a suitable catalytic system may be challenging when both H<sub>2</sub> and a poor oxidant must be activated. Beyond

classical hydrogenation methodologies aiming at reducing carbonyl derivatives, which have witnessed tremendous developments since the 1995 Noyori's report,<sup>15</sup> the reduction of more oxidized functional groups with H<sub>2</sub>, such as carboxylic acids, esters, amides, carbonates or CO<sub>2</sub>, has proved difficult, because of the low electrophilicity of these substrates and the need to promote successive hydride transfers.<sup>16</sup> For example, the first reports of a general homogeneous hydrogenation of unactivated esters were only unveiled independently in 2006 and 2007 by the Milstein's and Saudan's groups (Scheme 2).<sup>17</sup> Both methodologies rely on the use of ruthenium complexes supported by a PNN pincer ligand (PNN = 2-(di-tert-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine) (**1**) or a bidentate amino-phosphine (**2**). In the latter case, the presence of two amino-phosphine residue coordinated to the ruthenium atom was found to be pivotal for the catalytic activity as related Noyori-type catalysts bearing diamine and diphosphine are completely inactive in the hydrogenation of esters, though they are efficient with ketones.<sup>18</sup> Interestingly, such developments may have an important impact in the reduction of renewable organics and the Milstein's catalyst has been successfully applied to the depolymerization of waste polyesters, such as polyethylene terephthalate (PET).<sup>19</sup> Replacing the ruthenium catalyst with an iron catalyst was achieved in 2014, simultaneously by the Beller's and Guan's groups, using a PNP-iron(II) complex (**3** in Scheme 2).<sup>20</sup> and with a manganese-based complex (**4**) more recently.<sup>21</sup>

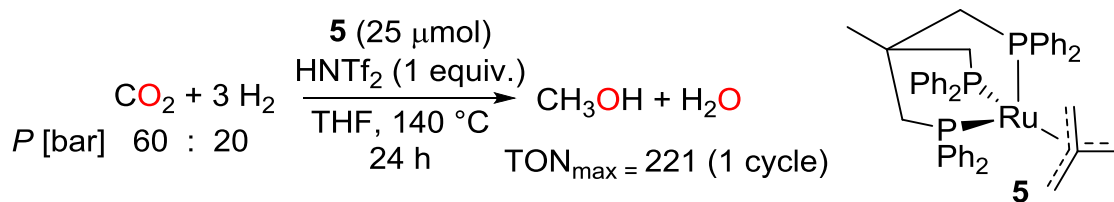


**Scheme 2. Hydrogenation of methyl benzoate catalyzed by ruthenium, iron or manganese-based complexes 1-4.**

The hydrogenation of  $\text{CO}_2$  is a laborious task because both  $\text{H}_2$  and  $\text{CO}_2$  are non-polar gases while the reduction products, namely formic acid, CO, methanol, water, etc., have an enhanced polarity and are thus potential poisons of the catalytic system. Thermodynamically, the hydrogenation of  $\text{CO}_2$  to formic acid, formaldehyde, CO and oxalic acid is endergonic, as reflected in the respective redox potentials of the couples involving  $\text{H}_2$  and  $\text{CO}_2$  (Scheme 1). For example, the hydrogenation of  $\text{CO}_2$  to formic acid is entropically disfavored ( $\Delta H^0 = -31.2 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta G^0 = +32.9 \text{ kJ}\cdot\text{mol}^{-1}$  at  $25 \text{ }^\circ\text{C}$  and  $\text{pH} = 0$ ) and common strategies to alleviate this thermodynamic hurdle require the use of a stoichiometric amount of a Brønsted base (for  $\text{NH}_3(\text{aq})$ ,  $\Delta H^0 = -84.3 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta G^0 = -9.5 \text{ kJ}\cdot\text{mol}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ) or highly polar solvents such as dimethylsulfoxide or water (in water,  $\Delta G^0 = -4.0 \text{ kJ}\cdot\text{mol}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ).<sup>22</sup> While the state-of-the-art is still dominated by noble metal based catalysts,<sup>23</sup> iron- or copper-based catalysts have emerged as potent candidates to promote this reaction.<sup>24</sup>



Even more challenging is the hydrogenation of CO<sub>2</sub> to methanol, which is a kinetically difficult yet slightly exergonic reaction ( $\Delta G^0 = -17.3 \text{ kJ}\cdot\text{mol}^{-1}$  at 25 °C and pH = 0).<sup>16d</sup> In 2012, Sanford et al. reported on an ingenious protocol based on cascade catalysis in order to address the inherent difficulty of the direct reduction of CO<sub>2</sub> in methanol.<sup>25</sup> More specifically, the authors developed a one-pot chemical sequence with three different catalysts, each of them being able to promote a single step within the sequence comprising the hydrogenation of CO<sub>2</sub> into formic acid followed by esterification of the latter into a formate ester and final hydrogenation of the ester to methanol. The compatibility between each catalyst is a significant hurdle of this approach and as a consequence a low TON of 2.5 for MeOH was obtained in a one-pot reaction. Later in 2012, Leitner, Klankermeyer et al. made a breakthrough in the hydrogenation of CO<sub>2</sub> to methanol with the robust [(triphos)Ru(TMM)] (**5**) complex (TMM=trimethylenemethane) in the presence of HNTf<sub>2</sub> as an acidic additive (Scheme 3).<sup>26</sup>

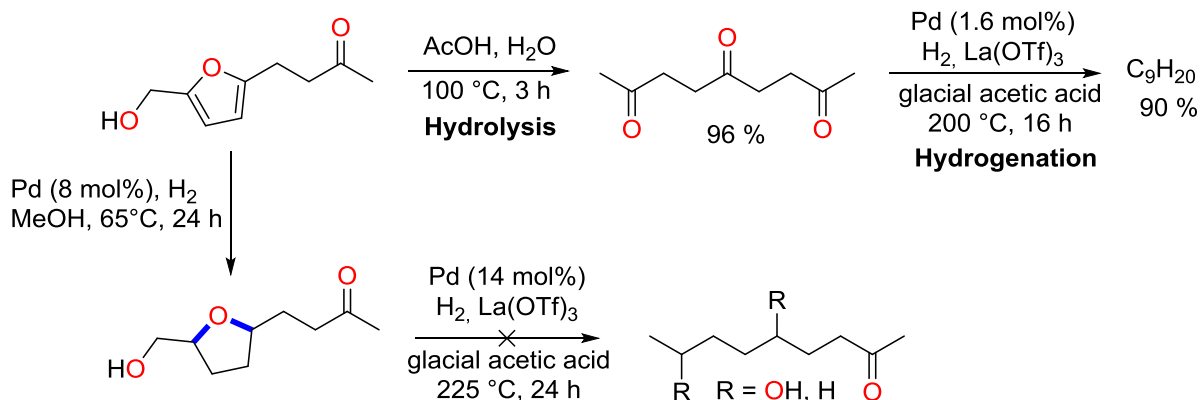


**Scheme 3. Hydrogenation of CO<sub>2</sub> catalyzed by the ruthenium complex [(triphos)Ru(TMM)] (**5**)**

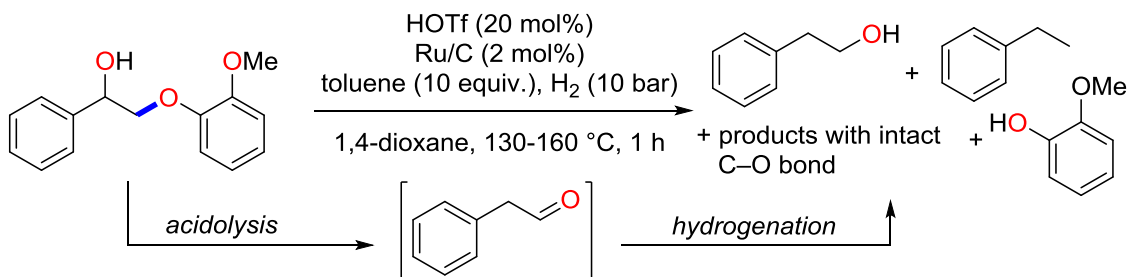
Using this catalytic system, a TON of 603 for MeOH production was obtained after 3 cycles at 140°C under pressure of CO<sub>2</sub> and H<sub>2</sub> (20 and 60 bar, respectively). To date, this homogeneous catalytic system is the sole to effect selectively the direct conversion CO<sub>2</sub> into MeOH and others have been explored, notably by Sanford, Milstein and Olah, to catalyze the hydrogenation of CO<sub>2</sub> derivatives, such as carbamates or carbonates formed by capture of CO<sub>2</sub> with amines or alcohols.<sup>27</sup>

H<sub>2</sub> is also a desirable reductant for the valorization of biomass or its waste products to produce fuels or chemicals.<sup>28</sup> In this context, a catalyst is also required to facilitate the deoxygenation of the organic reagent with H<sub>2</sub> and a significant kinetic challenge arises for the reduction C–O  $\sigma$  bonds (in blue in Scheme 4). A recent example from Sutton, Gordon et al. showed that the complete hydrogenation of extended furfural derivatives could be carried out with palladium on charcoal in the presence of a Lewis acid (namely La(OTf)<sub>3</sub>), when the furan ring is opened by hydrolysis prior to the reduction step (20 bar H<sub>2</sub> at 200 °C).<sup>29</sup> Similarly, de Vries, Barta *et al.* disclosed that the reductive cleavage of a model compound of the lignin  $\beta$ -O-4 linkage and the depolymerization of lignin itself (extracted from walnut shells by a dioxosolv procedure) actually proceeds *via* a sequence starting with the acidolysis of the C–O  $\sigma$  bond with triflic acid (TfOH) and the subsequent reduction of the transient aldehyde to the corresponding alcohol by hydrogenation catalyzed with Ru/C (Scheme 4, bottom).<sup>30</sup>

**Sutton, Gordon *et al.*:**



**de Vries, Barta *et al.*:**



**Scheme 4. Strategies to the complete reduction of furfural derivatives to the corresponding alkanes using hydrogenation methods (top) and reductive cleavage of lignin  $\beta$ -O-4 model compound by catalytic acidolysis and hydrogenation (bottom)**

Overall, these selected examples highlight the thermodynamic and current kinetic limitations of H<sub>2</sub> in the reduction of renewable compounds. The latter can be overcome at the price of catalysts design whose ultimate goal is to realize the potential of H<sub>2</sub> as the most atom-economical reductant in low pressure hydrogenations (e.g. 1 atm). Although state-of-the-art catalysts still rely on noble metals, increasing efforts are devoted to develop earth abundant or metal-free catalysts in the hydrogenation of poorly electrophilic substrates such as carboxylic acid derivatives.<sup>31</sup> These difficulties also translate into the use of high pressures of H<sub>2</sub> and elevated reaction temperatures. Specialized apparatus and thorough safety precautions are therefore needed to carry out such reductions. In addition, high pressures are often synonymous of large excess of hydrogen thus leading to low faradaic efficiencies, though the excess of H<sub>2</sub> can be recycled rather than vented. Using non-gaseous surrogates of H<sub>2</sub> may alleviate these drawbacks as well as provide opportunities to devise new selectivities in reductive processes.

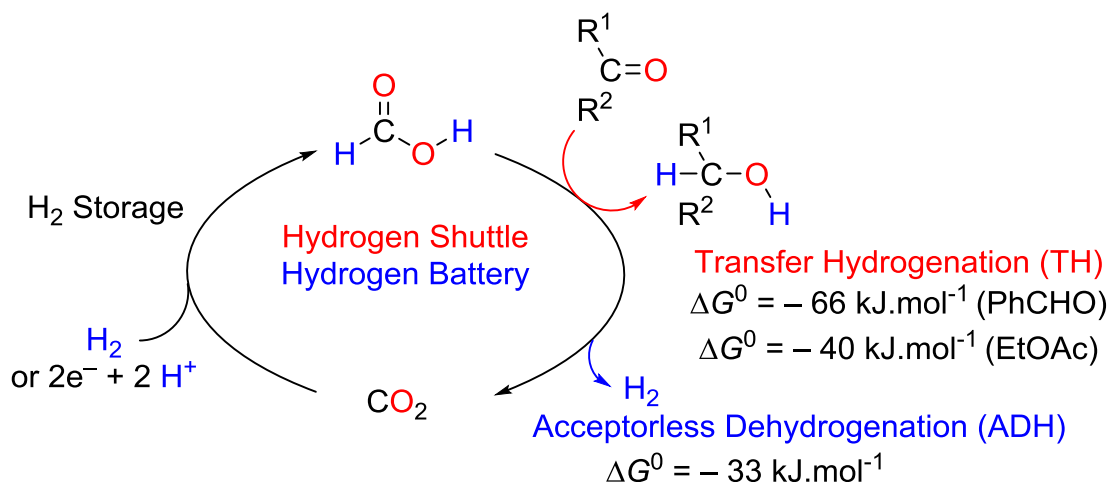
### 3. Transfer hydrogenation with formic acid as a hydrogen donor

Formic acid (HCO<sub>2</sub>H, FA) is a mild reductant with a slightly lower reduction potential than H<sub>2</sub> ( $E_{(CO_2/HCO_2H)}^0 = -0.17\text{ V}$  at pH = 0 vs. NHE) that ensures favorable thermodynamic balance for the reduction of most oxidants (Scheme 1). These reductive properties have early been recognized in non-catalytic reductive aminations such as the Eschweiler–Clarke or Leuckart–Wallach reactions.<sup>32</sup> In these transformations, FA delivers a synthetic equivalent of H<sub>2</sub> with concomitant release of CO<sub>2</sub>. FA is currently produced industrially from fossil sources by

carbonylation of methanol and subsequent hydrolysis of methyl formate with a market size of about 697 kt/year in 2013.<sup>33</sup> Yet, alternative protocols have become increasingly popular to access FA from renewable resources. For instance, Wasserscheid *et al.* have developed a Keggin-type polyoxometalate catalyst able to oxidize water-soluble carbohydrates, derived from biomass, with O<sub>2</sub> to yield FA and CO<sub>2</sub> (OxFA process).<sup>34</sup> More interestingly, FA can also be obtained by the 2-electron reduction of CO<sub>2</sub> either through CO<sub>2</sub> hydrogenation (*vide supra*) or electrolysis.<sup>35</sup> Importantly, the electrolysis of CO<sub>2</sub> to FA is currently under pilot development and shows great promise as relatively low overpotentials, high faradaic efficiencies and selectivities have already been achieved.<sup>36</sup>

Formic acid features ideal thermodynamic data to promote hydride transfer and this reductant could be considered as renewable in the short run, in agreement with the specifications defined in the first section of this Viewpoint. From a kinetic perspective, the polarized C–H bond in FA (BDE = 96 kcal.mol<sup>-1</sup>)<sup>13</sup> is 8 kcal.mol<sup>-1</sup> weaker than the H–H bond and therefore easier to activate at a metal center. In this respect, Watanabe *et al.* reported in 1981 the first transfer hydrogenation (TH) of carbonyl compounds with an equimolar amount of neat FA in the presence of the ruthenium complex RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> as catalyst (0.06 mol%).<sup>37</sup> While several aliphatic and aromatic ketones and aldehydes are effectively reduced at 125 °C after 3 h, the reaction was carried out in closed vessels and mechanistic investigations pointed out the likely involvement of H<sub>2</sub> as being the actual reductant. Indeed, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> was also shown to promote the hydrogenation of acetophenone under identical reaction conditions and a build-up of pressure (up to 120 bar) that corresponds to the dehydrogenation of FA into CO<sub>2</sub> and H<sub>2</sub> preceded the formation of 1-phenylethanol by reduction. This example is illustrative of the intricacy in play between hydrogenation and *apparent* transfer hydrogenation (from a

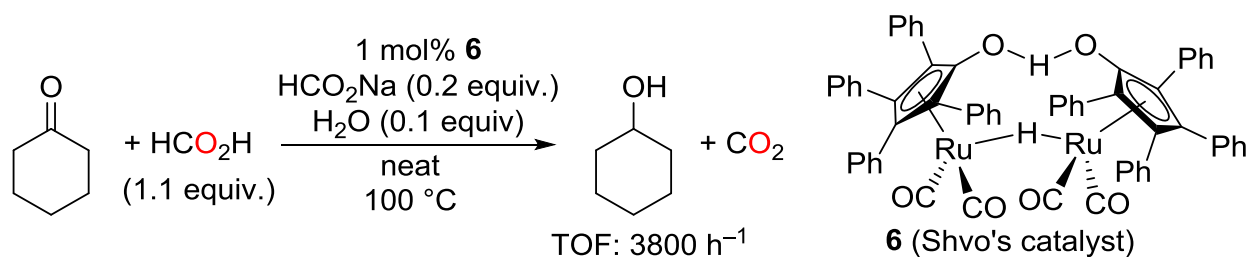
mechanistic standpoint) due to the facile acceptorless dehydrogenation of FA (ADH) that generates H<sub>2</sub>. In fact, a wide variety of transition metal complexes<sup>38</sup> can catalyze the ADH of FA or its derivatives such as sodium formate or the azeotrope 5 FA/2 NEt<sub>3</sub>, including iridium,<sup>39</sup> iron<sup>40</sup> and copper<sup>41</sup> complexes, and more recently also main group elements-based molecular compounds<sup>42</sup> (A1 and B) were shown to promote this reaction. The large collection of competent catalysts active in the decomposition of FA compared to those active in TH with FA suggests that the kinetics of the former process is relatively favorable. In fact, the TH of carbonyl or esters into the corresponding alcohols with FA ( $\Delta_r G_{PhCHO}^0 = -66 \text{ kJ.mol}^{-1}$ ;  $\Delta_r G_{EtOAc}^0 = -40 \text{ kJ.mol}^{-1}$  at 298 K for one mole of HCO<sub>2</sub>H) is thermodynamically favored over the acceptorless dehydrogenation ( $\Delta_r G^0 = -33 \text{ kJ.mol}^{-1}$  at 298 K) but is kinetically challenging when the proton of formic acid competes as an oxidant (Scheme 5).



**Scheme 5. Synthesis of FA by hydrogenation or electrolysis of CO<sub>2</sub> and kinetic competition between TH and ADH.**

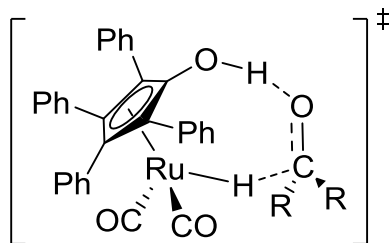
A milestone in TH reactions with FA was reached with the development of bifunctional catalysts,<sup>43</sup> which allow the minimization of both the ADH pathway and/or the subsequent

hydrogenation of the substrate that are likely involved in Watanabe's pioneering example. In fact, the necessity to discover catalysts that selectively promote TH over other side reactions is of paramount importance to realize the potential of FA as a sustainable reductant able to complement H<sub>2</sub> with potentially unprecedented selectivities (regio-, chemo- or stereoselectivities). In 1995, Shvo et al. reported that the cyclopentadienone-ligated ruthenium carbonyl complex  $\{[\text{Ph}_4(\eta^5\text{-C}_4\text{CO})_2\text{H}]\text{Ru}_2(\text{CO})_4(\mu\text{-H})\}$  (**6**) enables the TH of unactivated ketones and aldehydes into the corresponding alcohols or formate esters at 100 °C in neat FA (Scheme 6).<sup>44</sup> The dehydrogenation of FA was not observed even after 24 h in the absence of the carbonyl reagent.



**Scheme 6. Transfer hydrogenation of cyclohexanone with FA catalyzed by Shvo's catalyst**

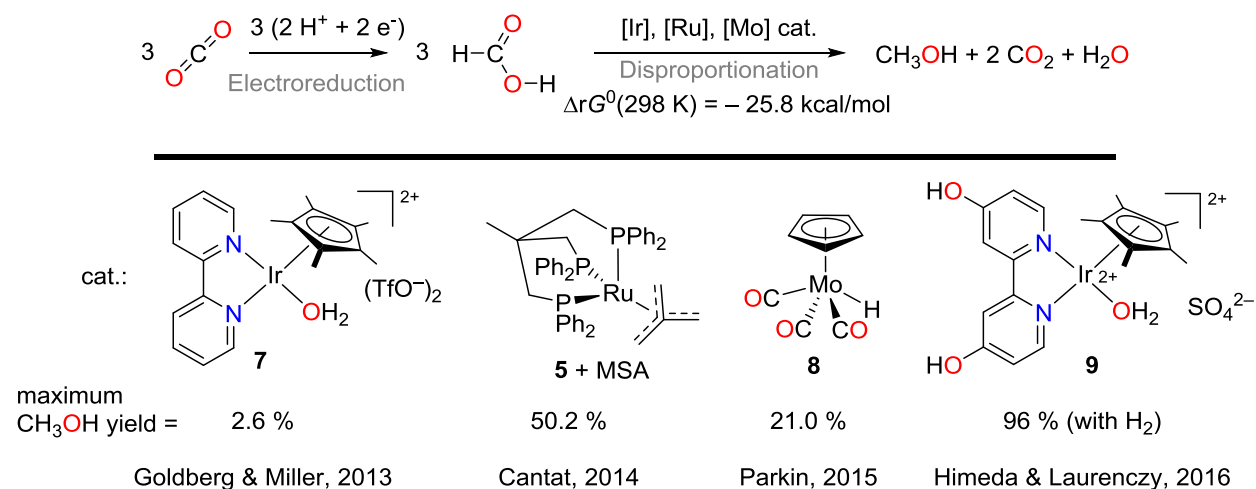
The inability of **6** to catalyze the acceptorless dehydrogenation of FA was further confirmed by Beller et al. in the course of their studies on the selective decomposition of FA/amine adducts.<sup>45</sup> This feature rules out the involvement of H<sub>2</sub> as hydride source during the reduction of carbonyls catalyzed by **6** and proves that the actual TH may outweigh ADH and/or hydrogenation through a proper catalyst design. A rationale for this peculiar behavior is based on the concerted transfer of a hydride and a proton respectively from the ruthenium center (Ru–H) and the hydroxycyclopentadienyl ligand (O–H) thereby lowering the kinetic barrier for the reduction of the carbonyl relatively to the DH (Scheme 7).<sup>46</sup>



**Scheme 7. Structure of proposed key transition state in transfer hydrogenation of ketones by Shvo's catalyst (6)**

While FA can reduce carbonyl derivatives through TH, the extension of this behavior to carboxylic acid derivatives remains largely unexplored either with FA or other hydrogen donors. Nevertheless, TH with FA can play a role in CO<sub>2</sub> reduction and a new strategy has been recently proposed to promote the 2-electron of CO<sub>2</sub> to FA and the subsequent disproportionation of FA to methanol, where FA is reduced by two other equivalents of FA *via* a formal TH (Scheme 8).<sup>47</sup> Although this approach offers an attractive alternative to the direct hexaelectronic reduction of CO<sub>2</sub> into MeOH, Miller, Goldberg *et al.* only unveiled in 2013 the first catalyst able to promote the disproportionation of FA to methanol, namely the iridium(III) cationic complex [Cp\*Ir(bpy)(OH<sub>2</sub>)](OTf)<sub>2</sub> (Cp\* = pentamethylcyclopentadienyl; bpy = 2,2'-bipyridine) (**7** in Scheme 8).<sup>48</sup> Using a low catalyst loading (< 0.008 mol%), MeOH was produced from aqueous FA solutions at 80 °C with yields of up to 2.6 % meaning that only 2.6 % of the C–H bonds originally present in reacted FA were preserved as C–H bonds in MeOH. Subsequently, Cantat *et al.* demonstrated that increased selectivity toward MeOH could be obtained with ruthenium(II) complexes as catalysts in combination with the triphos ligand and yields up to 50 % were achieved in the presence of an acidic additive (MSA, methanesulfonic acid), in THF at 150 °C.<sup>47</sup> Importantly, Parkin *et al.* disclosed the first catalysts containing the nonprecious metal

molybdenum and selectivities up to 21 % were reached with the molybdenum(II) complex CpMo(CO)<sub>3</sub>H (**8**) (Cp = cyclopentadienyl) in benzene at 100° C.<sup>49</sup>



### Scheme 8. Alternative strategy for the production of methanol *via* catalytic disproportionation of FA

In all the above examples, H<sub>2</sub> is in fact produced in at least 50 % yield *via* the competing DH of FA. In fact, mechanistic investigations performed on **5** showed that the selectivity is under thermodynamic control, the decarboxylation of formate being rate determining. The disproportionation of FA thus proceeds both via TH and hydrogenation and methanol production is favored under high pressure of H<sub>2</sub> and CO<sub>2</sub> (i.e. high FA concentration under isochoric conditions) and low temperature ( $\Delta_r H_{Disprop.}^0 = -12.3 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\Delta_r H_{DH}^0 = +31 \text{ kJ} \cdot \text{mol}^{-1}$  at 298 K for one mole HCO<sub>2</sub>H). These findings were further confirmed recently by Himeda, Laurency *et al.* who showed that the water-soluble complex [Cp\*Ir(bdhbp)(OH<sub>2</sub>)] [SO<sub>4</sub>] (**9**) catalyzes the disproportionation of aqueous FA, at 50 °C, with selectivities up to 96 % (at 98 % FA conversion) when the reaction was carried out under initial H<sub>2</sub> pressure (50 bar) in the presence of excess H<sub>2</sub>SO<sub>4</sub>.<sup>50</sup>



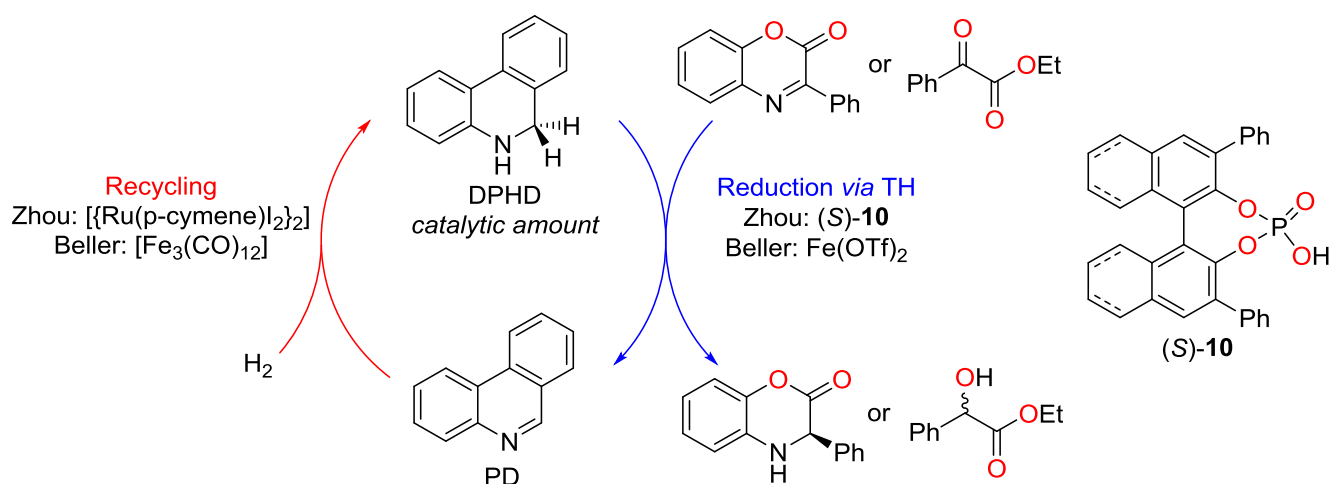
Overall, these examples show that, although formic acid complies nicely with the specifications depicted in Scheme 1, its fast decomposition to H<sub>2</sub> and CO<sub>2</sub> hampers the kinetic advantage of the polarized C–H in FA. We thus foresee that catalysts design is still needed to promote a true transfer hydrogenation of FA to carboxylic acid derivatives.

#### 4. Bio-inspired and renewable hydride donors

Reduction reactions are key processes in multi-electronic transformations catalyzed by metalloenzymes and bio-inspiration can serve as a guide to mimic hydride donors used by Nature, such as the reduced cofactors nicotinamide adenine dinucleotide, NADH, and its phosphorylated analog nicotinamide adenine dinucleotide phosphate, NADPH. For example, lactate dehydrogenase catalyzes the reduction of pyruvate into (*R*)-lactate by oxidation of NADH to NAD<sup>+</sup>. The sustainability of the reductive metabolism hinges on the continuous supply of electrons and protons from small molecules (*fuels*) such as H<sub>2</sub> or formate, which play the role of hydride *shuttles* to regenerate NADH from NAD<sup>+</sup>. In fact, NADH can be recycled from NAD<sup>+</sup> by decarboxylation of a formate anion and subsequent hydride transfer catalyzed by the NAD<sup>+</sup>-dependent formate dehydrogenase (FDH).

Several synthetic equivalents of cofactors containing the 1,4-dihydropyridine scaffold have been devised and their regeneration through transition-metal-based catalysis with H<sub>2</sub> or formates studied.<sup>51</sup> The reduction chemistry of the foremost NAD(P)H analogs, namely Hantzsch esters (HEH) and 1-benzyl-1,4-dihydronicotinamide (BNAH), has also been widely explored with either organo- or transition metal-based catalysts.<sup>52</sup> Thermodynamically, these reductants are well poised for the reduction of diverse C–O and C=O bonds ( $(E_{(BNA^+/BNAH)}^0 = -0.36 \text{ V vs. NHE})$ ) (Scheme 1).<sup>53</sup> From a catalysis viewpoint, biomimetic reductions have been reported that

regenerate *in-situ* the reduced NAD(P)H mimics with non-enzymatic systems.<sup>54</sup> For example, Zhou *et al.* developed a chiral phosphoric acid-catalyzed (CPA) highly enantioselective TH of various azaheterocycles with 9,10-dihydrophenanthridine (DHPD) as the *catalytic* reductant (Scheme 9).<sup>55</sup> The latter is continuously regenerated *via* an orthogonal hydrogenation of the oxidized phenanthridine (PD) catalyzed by [ $\{\text{Ru}(p\text{-cymene})\text{I}_2\}_2$ ]. Beller *et al.* also reported a conceptually-related TH of  $\alpha$ -ketoesters and  $\alpha$ -iminoesters catalyzed by two iron-based catalysts in the presence of a catalytic amount of DHPD and H<sub>2</sub> as the terminal reductant.<sup>56</sup> Although these features may pave the way to renewable chemical reduction with NAD(P)H analogs, examples of reduction of C=O bonds with such reductants remain scarce.



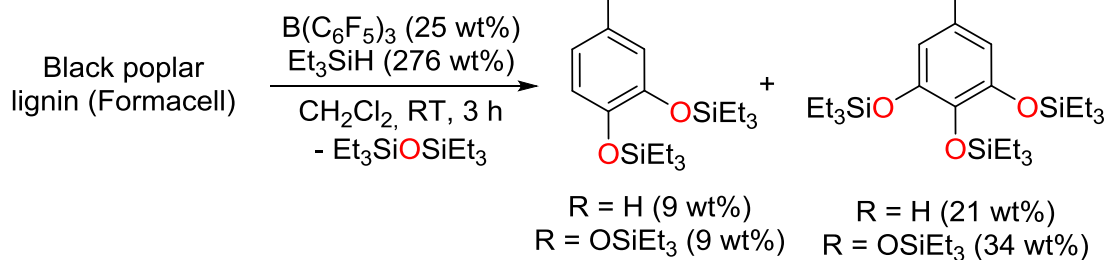
**Scheme 9. Catalytic transfer hydrogenation of benzoxazinones (Zhou *et al.*) and  $\alpha$ -ketoesters (Beller *et al.*) with continuous regeneration of the reductant (DHPD) by catalytic hydrogenation**

## 5. Hydrosilane and hydroborane reductants in C–O bond reduction

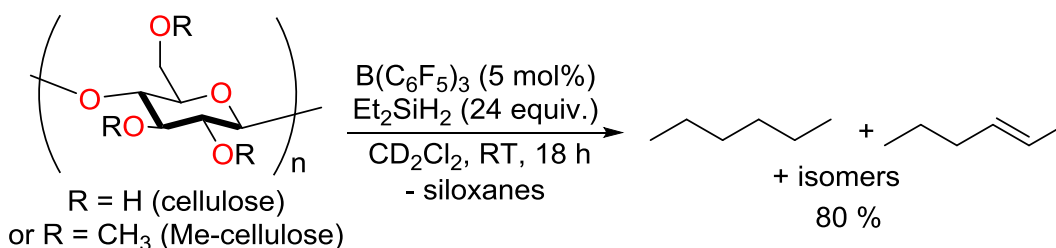
Hydrosilanes ( $\text{R}_3\text{SiH}$ ) and hydroboranes ( $\text{R}_2\text{BH}$ ) are attractive reductants in CO<sub>2</sub> and biomass conversion because they combine interesting thermodynamic and kinetic properties. Indeed, their redox potential falls in the range of  $-0.5$  to  $0$  V ( $E^\circ(\text{B}(\text{OMe})_3/\text{HB}(\text{OMe})_2) = -0.54$  V and

$E^\circ((\text{Me}_3\text{Si})_2\text{O})/\text{Me}_3\text{SiH} = -0.1 \text{ V vs NHE}$ )<sup>8</sup> and these values can be modulated by changing the nature of the substituents at the boron and silicon centers. Different hydroboranes and hydrosilanes are commercially available and some of them, like polymethylhydrosiloxane (PMHS) or tetramethyldisiloxane (TMDS) are cost efficient, non-toxic and stable towards oxygen and moisture.<sup>57</sup> In addition, they feature relatively weak and polarized Si–H and B–H bonds ( $\text{BDE}_{\text{Si-H}} = 95 \text{ kcal.mol}^{-1}$  in  $\text{Me}_3\text{Si-H}$  and  $\text{BDE}_{\text{B-H}} = 75 \text{ kcal.mol}^{-1}$  in  $\text{H}_2\text{B-H}$ ) compared to  $\text{H}_2$ .<sup>58</sup> Recent examples of  $\text{CO}_2$  hydrosilylation and hydroboration reactions have demonstrated that  $\text{CO}_2$  can be reduced to the formate or methoxide level under very mild conditions, at room temperature and under 1 bar  $\text{CO}_2$ , using a range of transition metal complexes and organic Lewis acids or bases as catalysts.<sup>59</sup> These results contrast with the hydrogenation of  $\text{CO}_2$ , which requires harsher conditions and special metal catalysts (*vide supra*). The mild reduction potential of hydrosilane is also a significant advantage to achieve enhanced chemoselectivity in reduction chemistry and this feature is of special interest for the valorization of highly heterogeneous materials such as natural lignin. In this respect, Cantat *et al.* have shown in 2015 that organosolv lignin extracted from hardwood or softwood can be efficiently depolymerized to isolable monoaromatic compounds with an unprecedented degree of convergence, using stoichiometric quantities of  $\text{Et}_3\text{SiH}$  and a catalytic amount of the potent Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>60</sup> A conceptually-related approach has also been reported by Gagné *et al.*, in which cellulosic carbohydrates are efficiently converted into a variety of aliphatic, deoxygenated hydrocarbons with diethylsilane ( $\text{Et}_2\text{SiH}_2$ ). Notably, 30 % methylated cellulose, which is more soluble than cellulose itself, was efficiently depolymerized into fully deoxygenated products with yields up to 80 % within 18 h (Scheme 10).<sup>61</sup>

**Cantat et al.:**



**Gagné et al.:**



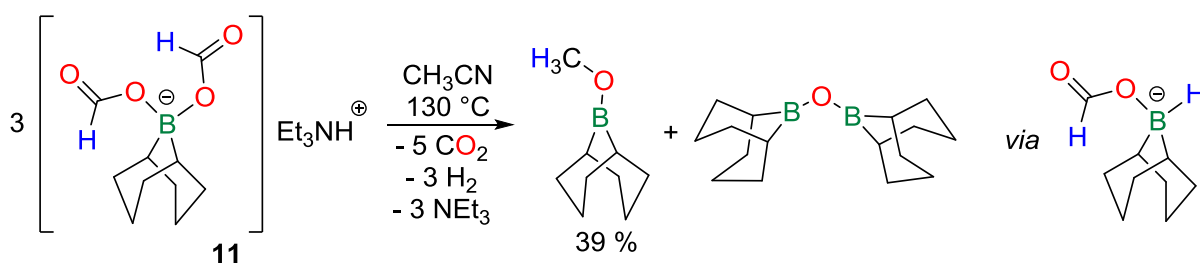
### Scheme 10. Catalytic depolymerization of lignin and cellulose by hydrosilylation

Of course, an important difference between hydrogenation and hydrosilylation/hydroboration methods derives from the formation of strong Si–O and B–O bonds in the products that shifts the reactions to the right, by formation of silyl or boryl formates and/or methoxides. In fact, the formation of oxidized silicon and boron products (e.g. silanols, siloxanes, boroxanes, etc.) represents the main drawback of this reduction strategy. Indeed, current methods for the recycling of siloxanes and boroxanes to hydrosilanes and hydroboranes, respectively, are very energy intensive. Despite the accessible reduction potential of the Si–O and B–O bonds, they notably involve strong reductants such as  $\text{LiAlH}_4$ . As such, hydrosilanes and hydroboranes are considered today as disposable hydrides that suffer from a low atom economy and their utilization in  $\text{CO}_2$  or biomass reduction will likely not yield any practical application. Nonetheless, they can serve as reductant to unveil new catalytic transformations for the recycling of  $\text{CO}_2$  to fine chemicals, which can then be transposed to other renewable reductants. A recent example of this strategy is the conversion of  $\text{CO}_2$  to methylamines which was first unveiled by

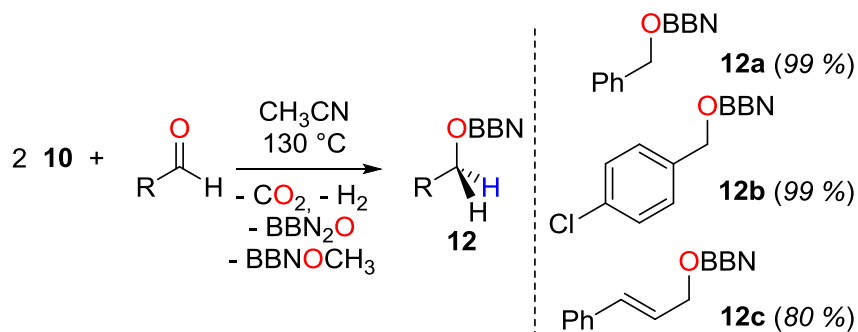
Cantat *et al.*<sup>62</sup> and Beller *et al.*<sup>63</sup> by reacting CO<sub>2</sub> with amines and hydrosilanes, before it was transposed to (transfer)hydrogenation with H<sub>2</sub> and FA.<sup>64</sup>

While hydrosilylation and hydroboration chemistry would benefit from a sustainable synthesis of hydrosilanes and hydroboranes from siloxanes and boroxanes, the utilization of surrogates of these reagents offers a possible alternative. In this context, Cantat *et al.* recently explored the reduction properties of silyl and boryl formates, which combine a renewable hydride source (HCO<sub>2</sub>) linked to the main group element. Bis(formoxy)dialkylborates R<sub>2</sub>B(OCHO)<sub>2</sub><sup>-</sup> (**11**) were shown to decarboxylate at 130 °C, to yield a borohydride intermediate R<sub>2</sub>B(H)(OCHO)<sup>-</sup> able to reduce formoxyboranes as well as aldehydes (Scheme 11).<sup>65</sup> These reactions formally correspond to a *transfer hydroboration* where the oxidant undergoes hydroboration by decarboxylation of the B–OCHO linkage and addition of the resulting B–H functionality across the C=O bond of the carbonyl.

Disproportionation of formate anions in the coordination sphere of boron:

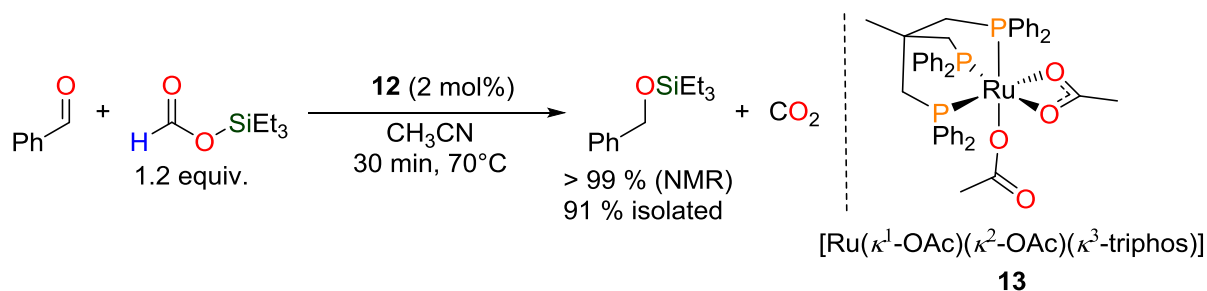


Application to the transfer hydroboration of non-enolizable aldehydes:



## Scheme 11. Disproportionation of formate anions in the coordination sphere of boron and application to the *transfer hydroboration* of aldehydes

In contrast to the anionic bis(formoxy)borates, silylformates are neutral and thermally stable molecules whose activation of both C–H and Si–O bonds requires a catalyst. Recently, we reported<sup>66</sup> that silylformates can be used as surrogates of various trialkylsilanes in the *transfer hydrosilylation* of aldehydes (Scheme 12).<sup>67</sup>



## Scheme 12. Transfer hydrosilylation of benzaldehyde with triethylsilyl formate catalyzed by well-defined ruthenium complex **13**

Detailed mechanistic investigations showed that a genuine hydrosilane is not formed during transfer hydrosilylation. Instead the ruthenium catalyst **13** promotes the reduction of the aldehyde through a sequence of decarboxylation of a formate ligand, hydride transfer to the oxidant and transmetallation. Importantly, silyl and boryl formates are non-protic reductants and can hence circumvent the unwanted dehydrogenation side-reaction encountered with FA. The recycling of siloxanes back to silyl formates has still to be demonstrated to show the sustainability of this class of reductant. It is nonetheless foreseeable that replacing the Si–O bond in siloxanes with a Si–O bond in silyl formates should be thermodynamically balanced.

## 6. Concluding remarks

The utilization of renewable carbon feedstocks, such as CO<sub>2</sub> or biomass, for the production of fuels and chemicals is a pressing challenge in chemistry and catalysis. It requires the development of efficient reduction methods aiming at deoxygenating these oxidized resources. Recent progress has shown that new chemical transformations can be devised to enlarge the scope of products available from CO<sub>2</sub> and lignin, for example. To translate these successes into practical applications, the nature of the reductant, utilized to promote C–O, bond cleavage is a hurdle as current reductants are based on fossil resources and/or are energy intensive. The ideal reductant combines thermodynamic and kinetic properties enabling the reduction of C–O and C=O bonds with a low overpotential and is produced from renewable energy and feedstocks. In this context, H<sub>2</sub> and formic acid are readily available candidates but their utilization imposes the design of efficient catalytic systems able to facilitate the (transfer) hydrogenation of reluctant substrates. In particular, catalysts active in the reduction of CO<sub>2</sub> and carboxylic acid derivatives by transfer hydrogenation with formic acid, without competing release of H<sub>2</sub>, are still to be developed. Bioinspired reductants, based on the NAD(P)H or FADH<sub>2</sub> cofactors, have been overlooked in the reduction of CO<sub>2</sub> and biomass although they could be useful reagents in the production of fine chemicals from renewables. Finally, hydrosilanes and hydroboranes have been extensively applied to CO<sub>2</sub> reduction over the last five years, thanks to their mild reduction potentials and increased reactivity towards oxygen-rich materials. Yet, these reductants should be considered as disposable due to their low atom economy. In addition, they currently suffer from production methods that are highly energy intensive. New strategies and synthetic methods aiming at producing hydrosilanes and hydroboranes from Si–O and B–O functionalities would offer an appealing achievement in hydrosilylation and hydroboration chemistry. These

challenges represent exciting research questions in which homogeneous and heterogeneous catalysis as well as organic chemistry are key.

## AUTHOR INFORMATION

### Corresponding Author

\*Thibault Cantat

[thibault.cantat@cea.fr](mailto:thibault.cantat@cea.fr)

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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