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# Catalytic synthesis of carboxylic acids from oxygenated substrates using CO<sub>2</sub> and H<sub>2</sub> as C1 building blocks†

Matilde V. Solmi,<sup>a</sup> Jeroen T. Vossen,<sup>a,b</sup> Marc Schmitz,<sup>a</sup> Andreas J. Vorholt <sup>b</sup> and Walter Leitner <sup>\*a,b</sup>

This work focuses on the development and investigation of a Rh/TPP catalytic system for the synthesis of saturated aliphatic carboxylic acids from readily available oxygenated substrates, H<sub>2</sub> and non-toxic, renewable CO<sub>2</sub>. Optimization of the reaction conditions and reagents was carried out using 2-butanol and 1-butanol as typical secondary and primary alcohols. Afterwards, the reaction system was investigated in-depth with a separate investigation of the reverse water–gas–shift–reaction and the carbonylation reaction as key steps of the overall tandem transformation. Based on these results, a reaction network was established with two distinct main pathways. While the secondary alcohols are converted preferentially *via* acid catalysed dehydration to the corresponding olefins followed by hydroxycarbonylation, the primary alcohols react primarily *via* nucleophilic substitution to the iodide compound followed by a Monsanto-type carbonylation. Based on these results, a broad range of alcohols including bio-based substrates was converted to the corresponding C1 elongated carboxylic acids. Additionally, other oxygenated substrates such as aldehydes, ketones and industrially relevant substrate mixtures were applied successfully.

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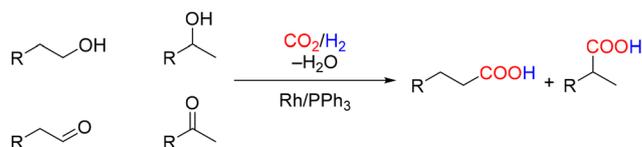
## 1. Introduction

Carboxylic acids and their derivatives are highly important for their synthetic utilization in the production of polymers, pharmaceuticals, solvents and food additives.<sup>1–5</sup> In particular, aliphatic mono-carboxylic acids are employed in the polymer industry,<sup>6,7</sup> in agrochemical applications, in the food and feed-stock industry,<sup>1,8</sup> as solvents<sup>1</sup> and as biofuels.<sup>9</sup> Industrially, aliphatic carboxylic acids (C<sub>4</sub>–C<sub>13</sub>) are mostly produced *via* an oxidation of the corresponding aldehydes, obtained from hydroformylation processes.<sup>1,10</sup> Other types of carboxylic acids are produced by a carbonylation of alcohols or alkenes (acetic acid, pivalic acid and propionic acid).<sup>1,11–14</sup> Further processes to obtain higher carboxylic acids from alcohols and carbon monoxide (CO) have been reported over the years by different research groups (from academia and industry) using both homogeneous and heterogeneous catalysts.<sup>11,15–34</sup> Overall, the current production of saturated aliphatic carboxylic acids is

limited to processes based mainly on toxic and mostly non-renewable CO.

CO<sub>2</sub> is a highly attractive renewable and non-toxic alternative to CO as a C1 building block. It can be used directly for carboxylations or in combination with “green” hydrogen as a reductant to provide *in situ* CO for carbonylations.<sup>35</sup> Several substrate classes have been converted to carboxylic acids using CO<sub>2</sub> as a C1 building block, such as boronic esters,<sup>36,37</sup> organohalides,<sup>38–41</sup> tosylates/mesyates,<sup>38,41</sup> alkenes<sup>42,43</sup> and dienes.<sup>44</sup>

Previously, our group reported a rhodium-based system, which produces carboxylic acids from simple alkenes with yields up to 91% using CO<sub>2</sub> and H<sub>2</sub> in a formal hydroxycarbonylation (Scheme 1). Mechanistic and labelling studies suggest the *in situ* formation of CO and H<sub>2</sub>O by a reverse Water–Gas Shift Reaction (rWGS), which occurs in hydroxycarbonylation.



**Scheme 1** Formal hydroxycarbonylation of oxygenated substrates (primary and secondary alcohols, ketones, aldehydes) with CO<sub>2</sub>, H<sub>2</sub> and Rh catalyst.<sup>45</sup>

<sup>a</sup>Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany

<sup>b</sup>Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34–36, 45470 Mülheim an der Ruhr, Germany. E-mail: walter.leitner@cec.mpg.de

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Similar to the catalytic systems used in the Monsanto process for the carbonylation of methanol to acetic acid, the reaction requires acidic conditions and an iodide promoter and  $\text{PPh}_3$  as a ligand.<sup>45</sup> The conversion of alcohols to carboxylic acids under these reaction conditions was also mentioned briefly in this preliminary study. Since then, Han *et al.* investigated the conversion of methanol to acetic acid with  $\text{CO}_2/\text{H}_2$  using Rh/NHC catalytic systems with LiI as a promoter<sup>46,47</sup> and Zhang *et al.* investigated the reaction with LiI as a promoter and iridium(III) acetate as a catalyst.<sup>48</sup>

Herein, we report the use of a Rh-based homogeneous catalytic system for the synthesis of carboxylic acids from various oxygenated substrates such as alcohols, ketones, aldehydes and mixtures of substrates with  $\text{CO}_2$  and  $\text{H}_2$ . The two reactions involved, rWGS and hydroxycarbonylation, will be studied in detail to investigate the reaction pathway and potential intermediates in the process. Based on the findings for the different substrate classes, a reaction network will be established, and the broad applicability will be demonstrated.

## 2. Results and discussion

Initial reactions were carried out with 2-butanol and 1-butanol as typical secondary and primary alcohols under a gas mixture of  $\text{CO}_2$  and  $\text{H}_2$  as carbonylating agents. The components of the catalytic system such as the Rh precursors,  $\text{PPh}_3$  as a ligand, and an acid ( $p\text{-TsOH}\cdot\text{H}_2\text{O}$ ) from a previous study<sup>45</sup> and  $\text{CHI}_3$  as an iodide compound were used as the starting point.

### 2.1 Optimization of the reaction parameters

2-Butanol was used as a secondary alcohol for optimizing the reaction conditions (Table 1) with the initial reaction conditions of 140 °C in 1 mL acetic acid, 2.4 mol%  $[\text{RhCl}(\text{CO})_2]_2$  with TPP as a ligand (Rh : P = 1 : 5), the Brønsted acid  $p\text{-TsOH}$  (Rh :  $p\text{-TsOH}$  = 1 : 3.5), an iodide source iodoform (Rh :  $\text{CHI}_3$  = 1 : 2.5), a hydrogen pressure of 10 bar and a  $\text{CO}_2$  pressure of 20 bar. The yield of target molecules, valeric acid (VA) and

2-methylbutanoic acid (2-MBA), was 45% with a VA-to-MBA ratio of 2 : 1 in the first experiment with over 99% conversion of the substrate alcohol (Table 1, entry 1). The obtained side products were the acetate, iodide, olefin and alkane.

Firstly, the influence of solvents and their volume on the reaction was studied. Neat conditions mainly lead to the formation of ethers in the presence of  $p\text{-TsOH}$ .<sup>49</sup> After a solvent screening (ESI, Table S1†), acetic acid turned out to be the best of the tested solvents with a total yield of 67%. The amount of solvent also influenced the reaction with 2 mL of acetic acid showing better results than 1 or 3 mL (Table 1, entries 1–3). The influence of  $p\text{-TsOH}\cdot\text{H}_2\text{O}$  on the yield of carboxylic acids is related to the amount of solvent. In 1 mL of acetic acid, the presence of  $p\text{-TsOH}\cdot\text{H}_2\text{O}$  does not have any influence on the carboxylic acid yield (ESI, Table S1†). The best result was obtained using 2 mL of acetic acid in the presence of  $p\text{-TsOH}\cdot\text{H}_2\text{O}$  (Table 1, entry 2), while the absence of the additive only led to traces of the desired product (Table 1, entry 4). This demonstrates that sufficient Brønsted acidity of the reaction medium is vital for the conversion. The influence of temperature in the range between 140 °C and 180 °C was tested afterwards, with the best result obtained at a temperature of 160 °C (Table 1, entries 2, 5 and 6). The yield of VA and 2-MBA rises to 77%, due to a reduced production of side products. A further increase to 180 °C results in a drop in carboxylic acid yield, probably due to a deactivation of the catalyst *via* ligand dissociation from the metal centre.

Reducing the  $\text{H}_2$ -pressure to 5 bar (Table 1, entry 7) or increasing it to 20 bar (Table 1, entry 8) caused a drastic reduction of the carboxylic acid yield. With the  $\text{H}_2$  pressure set at 10 bar, a screening of the  $\text{CO}_2$  pressure was carried out (10–30 bar, ESI, Table S1†). 20 bar of  $\text{CO}_2$  was chosen for further studies, because no significant improvement could be reported for any other pressure. With these reaction parameters further experiments on the  $\text{CHI}_3$  and  $\text{PPh}_3$  amounts and Rh precursor were performed which can be found in the ESI, Table S2.†<sup>50</sup> Under the optimized reaction conditions, a yield of 77% of carboxylic acids with a 2 : 1 ratio of VA : 2-MBA was obtained.

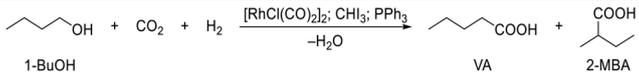
**Table 1** Hydroxycarbonylation of 2-BuOH with  $\text{CO}_2$  and  $\text{H}_2$ : influence of different reaction parameters

Entry	Volume of acetic acid (ml)	$p\text{-TsOH}\cdot\text{H}_2\text{O}$ (mol mol <sub>Rh</sub> <sup>-1</sup> )	Temperature (°C)	$\text{H}_2$ -pressure (bar)	Carboxylic acid yield (%)
1	1	3.5	140	10	45
2	2	3.5	140	10	67
3	3	3.5	140	10	8
4	2	—	140	10	2
5	2	3.5	160	10	77
6	2	3.5	180	10	66
7	2	3.5	160	5	26
8	2	3.5	160	20	26

If not specified, conversion is over 99%, the VA/2-MBA ratio is about 2/1 and the mass balance is around or above 80%. Reaction conditions: 1.88 mmol 2-BuOH, 46 μmol  $[\text{RhCl}(\text{CO})_2]_2$ , acetic acid as solvent, 2.5 mol mol<sub>Rh</sub><sup>-1</sup>  $\text{CHI}_3$ , 5 mol mol<sub>Rh</sub><sup>-1</sup>  $\text{PPh}_3$ , and 20 bar  $\text{CO}_2$ .



**Table 2** Hydroxycarbonylation of 1-BuOH with CO<sub>2</sub> and H<sub>2</sub>: influence of different reaction parameters



1-BuOH + CO<sub>2</sub> + H<sub>2</sub>  $\xrightarrow[-H_2O]{[RhCl(CO)_2]_2; CHI_3; PPh_3}$  VA + 2-MBA

Entry	Volume of acetic acid (ml)	<i>p</i> -TsOH·H <sub>2</sub> O (mol mol <sub>Rh</sub> <sup>-1</sup> )	Temperature (°C)	H <sub>2</sub> -pressure (bar)	Carboxylic acid yield (%)
1	1	3.5	140	10	30
2	2	3.5	140	10	35
3	3	3.5	140	10	3
4	1	—	140	10	44
5	2	—	140	10	2
6	2	3.5	160	10	26
7	1	—	160	10	59
8	1	—	180	10	47
9	1	—	160	5	44
10	1	—	160	20	64
11	1	—	160	30	56

If not specified, conversion is over 99%, the VA : 2-MBA ratio is about 2 : 1 and the MB is around or above 80%. Standard reaction conditions: 1.88 mmol 1-BuOH, 46 μmol [RhCl(CO)<sub>2</sub>]<sub>2</sub>, acetic acid as solvent, 2.5 mol mol<sub>Rh</sub><sup>-1</sup> CHI<sub>3</sub>, 5 mol mol<sub>Rh</sub><sup>-1</sup> PPh<sub>3</sub>, and 20 bar CO<sub>2</sub>.

The corresponding primary alcohol 1-BuOH was also investigated to determine the influence of the electronic structure of the alcohol group (Table 2). Tables with solvent, precursor and parameter screening can be found in the ESI (Tables S3 and S4†). The solvent screening shows similar trends to that for 2-BuOH with the best yield obtained in acetic acid. In contrast to the secondary alcohol, however, higher carboxylic acid yields were obtained for the primary alcohols without *p*-TsOH·H<sub>2</sub>O (Table 2, entry 4). This became even more apparent when increasing the temperature from 140 °C to 160 °C: the yield of carboxylic acids decreased from 35% to 26% if *p*-TsOH·H<sub>2</sub>O was present, while it increased to 59% if *p*-TsOH·H<sub>2</sub>O was omitted (Table 2, entry 6–8). This may be due to an increased formation of side products, in particular *n*-butyl ester, at a higher temperature in the presence of *p*-TsOH·H<sub>2</sub>O.<sup>49</sup> The pressure also showed a significant influence as a hydrogen pressure of 20 bar increased the yield, whereas it reduced the yield for 2-BuOH (Table 2, entry 9–11). The highest yield of 64% (VA : 2-MBA = 2 : 1) was obtained with 1 mL acetic acid, 20 bar H<sub>2</sub>, without *p*-TsOH·H<sub>2</sub>O at 160 °C (Table 2, entry 10).

## 2.2 Investigating the reaction network

After optimising the reaction conditions, a more detailed investigation of the reaction, its products and side products as well as the individual reaction steps combined in the reaction was performed. The catalytic system composed of a rhodium complex, PPh<sub>3</sub> and CHI<sub>3</sub> in acetic acid is known to catalyse the synthesis of carboxylic acids from olefins with CO<sub>2</sub> and H<sub>2</sub> *via* a reverse water-gas-shift-reaction (rWGSR) step, followed by a hydroxycarbonylation of the olefin with CO and H<sub>2</sub>O produced *in situ*.<sup>45</sup> Starting from alcohols as substrates, the carbonylation can be envisaged to occur alternatively at an alkyl iodide intermediate formed from the alcohol and the iodide source akin to the Monsanto process for methanol. Consequently, the following section is divided into three parts: (i) the rWGSR

step, (ii) the subsequent carbonylation step and (iii) the overall reaction network.

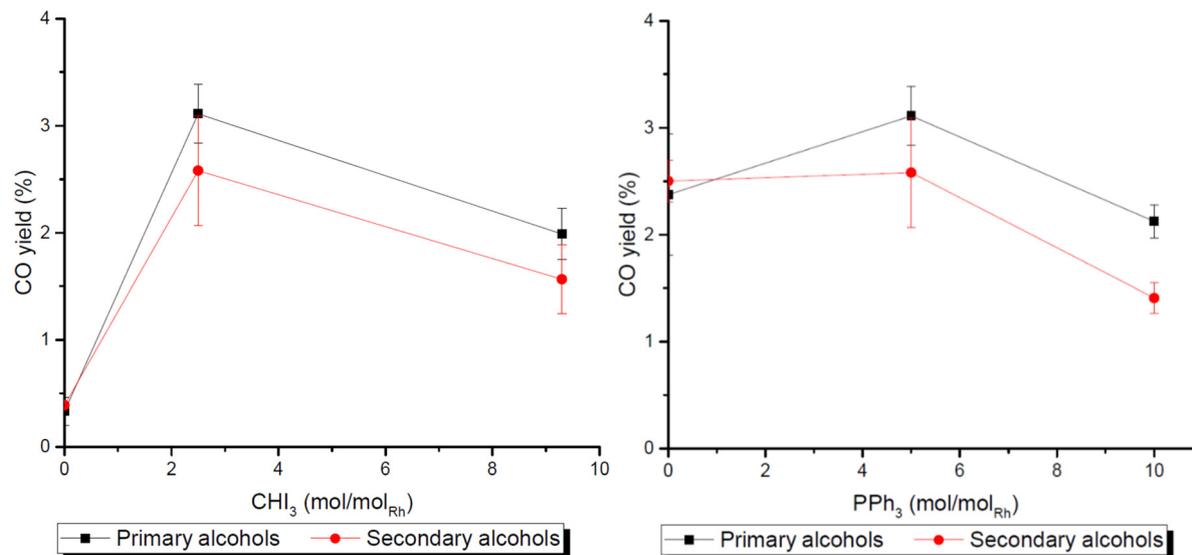
**2.2.1 Reverse water gas shift reaction step.** The first step of the reaction is the transformation of CO<sub>2</sub> and H<sub>2</sub> into CO and H<sub>2</sub>O. A quantitative analysis of the rWGSR occurring in the system allowed for an investigation of the influence of the CHI<sub>3</sub> and PPh<sub>3</sub> additives and of the precursor oxidation state on this step.

The rWGSR was tested by using the optimized conditions for either primary or secondary alcohols. The resulting gas phase was collected in a gas bag and analysed by GC. A CO yield of 2.6% was obtained for secondary alcohols and 3.1% for primary alcohols. The relatively high yield given the comparatively low reaction temperature for the rWGSR (Fig. 1) is largely due to the operation in the condensed phase. The same experiments were carried out in the absence of the precursor, demonstrating the catalytic role of the rhodium metal component (ESI, Table S9†).

The effect of the amount of CHI<sub>3</sub> and PPh<sub>3</sub> on the rWGSR was investigated (Fig. 1). CHI<sub>3</sub> is required for the CO<sub>2</sub> conversion to occur, as also reflected in the overall reaction system which barely shows any conversion without CHI<sub>3</sub> (ESI, Fig. S4–S7†). However, large amounts reduce the CO yield, which may be due to the formation of inactive catalyst species at high I<sup>-</sup> concentrations. The phosphine ligand PPh<sub>3</sub> has little influence on the rWGSR and presumably acts mainly as a stabilizing ligand for Rh species at low CO pressures.

**2.2.2 Carbonylation reaction step.** Subsequently, the role of CO *vs.* CO<sub>2</sub> for the C1 elongation was addressed. Labelled <sup>13</sup>C<sup>18</sup>O was used to investigate whether CO rather than CO<sub>2</sub> is incorporated into the product even if it is highly diluted in CO<sub>2</sub>. The experiment was performed using 2-BuOH and 1-BuOH as substrates with their corresponding optimized conditions. The gas mixture was formed by CO<sub>2</sub> and H<sub>2</sub> with the amounts normally used to perform these reactions and additional <sup>13</sup>C<sup>18</sup>O (2 bar). H<sub>2</sub>O was added in a 1 : 1 amount with respect to the <sup>13</sup>C<sup>18</sup>O used, representing the stoichiometry of the





**Fig. 1** Influence of different amounts of  $\text{CHI}_3$  (left) and  $\text{PPh}_3$  (right) on the CO yield (rWGSR) using the optimized conditions for primary alcohols and secondary alcohols. Reaction conditions: 1.88 mmol butanol, 92  $\mu\text{mol}$  Rh, 1 ml of acetic acid for primary alcohols, 2 mL acetic acid for secondary alcohols, 3.5 mol  $\text{mol}_{\text{Rh}}^{-1}$   $p\text{-TsOH}\cdot\text{H}_2\text{O}$  for 2-butanol,  $\text{CHI}_3$ ,  $\text{PPh}_3$ , 20 bar  $\text{CO}_2$ , 20 bar  $\text{H}_2$ , 160  $^\circ\text{C}$ , and 16 h. Yields were calculated on the total amount of  $\text{CO}_2$  pressurized in the reactor (22.7 mmol).

rWGSR. GCMS measurement showed that both  $^{13}\text{C}$  and  $^{12}\text{C}$  were incorporated into the acid product after 2 h of reaction. The  $^{13}\text{C}$  NMR spectra obtained starting from 1-butanol and the ratio between the areas is reported in the ESI (Fig. S8 and Table S8,† approximately  $\text{COOH}:\text{CH} = 25:1$ ). The ratio between the integrals did not change from 2 h to 16 h of reaction time which implies that the added  $^{13}\text{C}$  is incorporated immediately during the first 2 h of the reaction. This finding indicates clearly the integration of both catalytic cycles – rWGSR of  $\text{CO}_2$  into CO and carbonylation with the formed CO – in the overall formation of the carboxylic acids.

Varying the amount of iodide additive in the carbonylation step shows the same results already observed for the rWGSR with the best yield at small amounts (Fig. 1 and ESI, Fig. S2†). Similar experiments were performed by varying the amount of  $\text{PPh}_3$  (Fig. 1 and ESI, Fig. S3†). In a reaction using CO and  $\text{H}_2\text{O}$  directly, the stabilizing ligand is not required to obtain the desired product as the CO stabilizes the complex, being readily available from the beginning of the reaction, unlike with  $\text{CO}_2$  and  $\text{H}_2$  where it has the stabilizing effect for the complex at low CO pressures. The maximum activity observed is obtained with 10 eq. of  $\text{PPh}_3$ . Increasing the amount of phosphine to 20 eq. results in a decrease of activity.

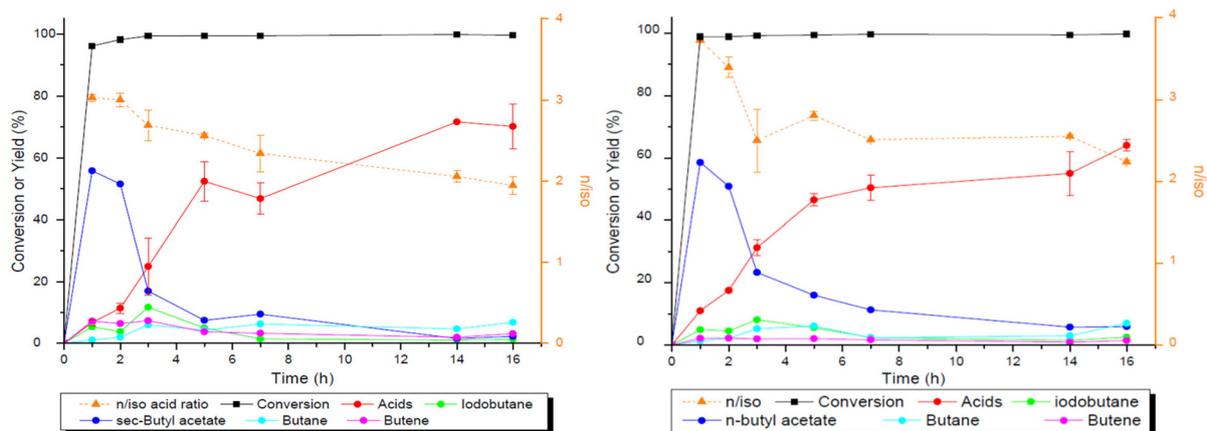
**2.2.3 Overall reaction network.** Taking a closer look at the time profile of the reaction to identify potential side products and intermediates, the conversion of 2-BuOH and 1-BuOH is near completion after 1 h (Fig. 2). In addition to the carboxylic acid products other components such as iodobutane, butenes, butane and butyl acetate are also formed during the reaction. Albeit the volatility of some of the components prevents a fully quantitative analysis, significant trends can be derived from the obtained data. For 2-BuOH a significant concentration of

butenes and iodobutane can be observed during the entire reaction. In the reaction of 1-BuOH, only small amounts of butenes are formed in comparison with that of iodobutane. The concentration of the other components remains relatively low throughout the reaction and decreases again at 16 h reaction time. Thus, the olefins and alkyl iodides appear to be possible key intermediates in the reaction.

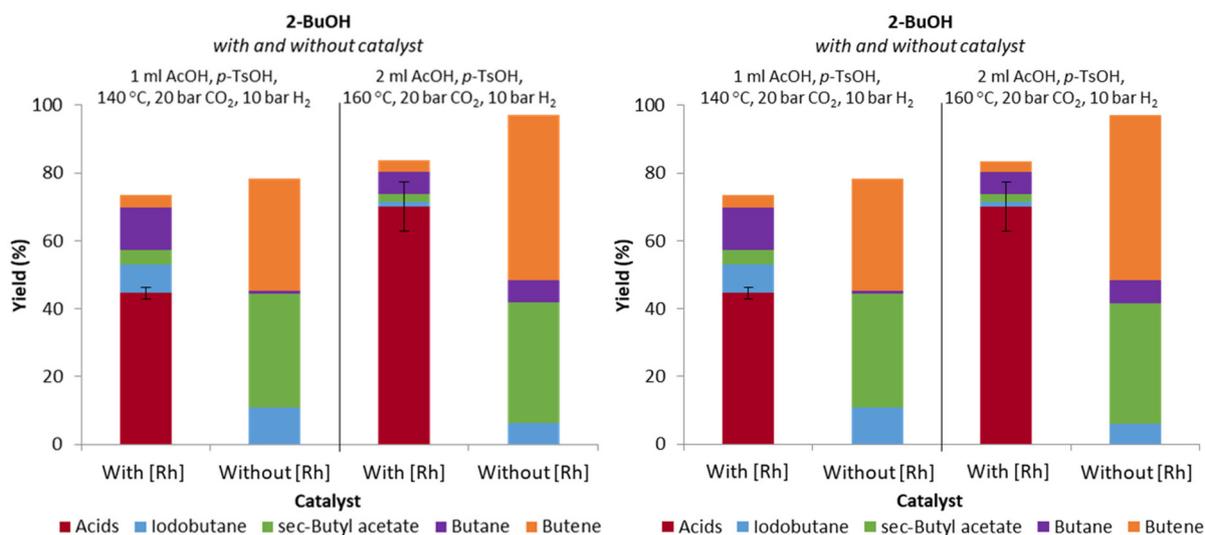
Blank tests without the catalyst were performed to see which reactions take place in the absence of the catalyst (Fig. 3). The corresponding iodide, acetate, alkane and olefin are formed in the absence of the transition metal catalyst. The olefin is formed preferentially over the iodide for 2-BuOH in comparison with that for 1-BuOH, reflecting that the dehydration of secondary alcohols is faster. 1-BuOH in turn forms more alkyl iodide, as the  $\text{S}_{\text{N}}2$  reaction is faster for primary alcohols in comparison with secondary alcohols.

Based on these investigations and results from the previous sections, an overall reaction network is proposed in Scheme 2. The alcohol can react *via* a first path in an  $\text{S}_{\text{N}}2$  reaction to form the iodide compound with an iodide source such as  $\text{CHI}_3$  or HI. The iodide can then react similarly to the Monsanto process by carbonylation forming iodic acid initially which cannot be detected as it is hydrolysed to the acid in the presence of water right away forming the carboxylic acid and HI. This path is more likely for primary alcohols as the  $\text{S}_{\text{N}}2$  reaction is faster in comparison with that for secondary alcohols. The alternative path occurs *via* the olefin through an acid catalysed dehydration of the alcohol, with the acetic acid solvent,  $p\text{-TsOH}\cdot\text{H}_2\text{O}$  and/or HI generating the required Brønsted acid. This step is more likely for secondary alcohols as they are dehydrated more easily than primary alcohols. The olefin can react in the carbonylation to form each of the acid product





**Fig. 2** Time profile of the reaction of 2-BuOH (left) and 1-BuOH (right) to form VA and 2-MBA. Reaction conditions: 2-BuOH: 1.88 mmol of 2-BuOH, 92  $\mu\text{mol}$  Rh, 2 ml of acetic acid, 2.5 mol  $\text{mol}_{\text{Rh}}^{-1}$  of  $\text{CHI}_3$ , 5 mol  $\text{mol}_{\text{Rh}}^{-1}$  of  $\text{PPh}_3$ , 3.5 mol  $\text{mol}_{\text{Rh}}^{-1}$   $p\text{-TsOH}\cdot\text{H}_2\text{O}$ , 20 bar  $\text{CO}_2$ , 10 bar  $\text{H}_2$ , and 160  $^\circ\text{C}$ . Reaction conditions: 1-BuOH: 1.88 mmol of 1-BuOH, 92  $\mu\text{mol}$  Rh, 1 ml of acetic acid, 2.5 mol  $\text{mol}_{\text{Rh}}^{-1}$  of  $\text{CHI}_3$ , 5 mol  $\text{mol}_{\text{Rh}}^{-1}$  of  $\text{PPh}_3$ , 20 bar  $\text{CO}_2$ , 20 bar  $\text{H}_2$ , and 160  $^\circ\text{C}$ . The mass balance for these reactions contains a gap due to the formation of highly volatile compounds such as butane and butene which are partially lost during the release of reaction pressure.



**Fig. 3** Comparison between the blank test and the results obtained with the pre-catalyst for the preliminary reaction conditions and the optimized conditions for 2-BuOH (left) and 1-BuOH (right).

isomers, and it can also isomerize in the presence of the rhodium catalyst. The internal olefin can only form iso-products. In the presence of hydrogen, the rhodium complex can also hydrogenate the olefin to the corresponding alkane.

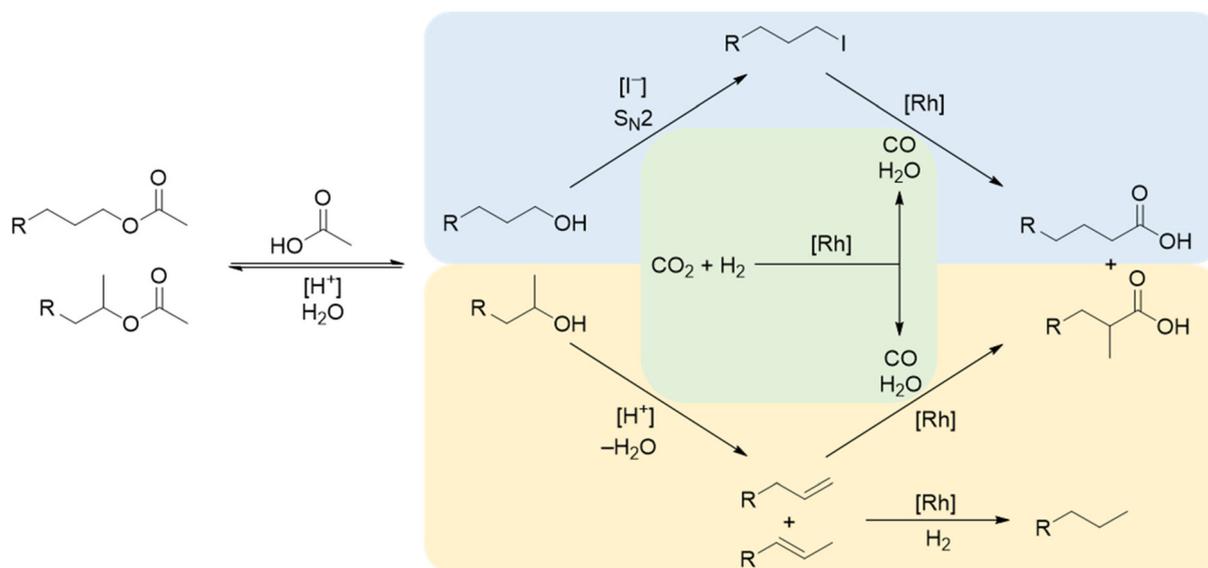
As observed in the screening experiments, without the iodide additive and without the acid additive  $p\text{-TsOH}\cdot\text{H}_2\text{O}$  or the acidic solvent acetic acid, the hydroxycarbonylation does not occur. This indicated that a direct reaction from the alcohols to the acids *via* a CO insertion is not possible and the reaction has to follow one of the two routes with iodoalkanes or olefins as intermediates. The acid-catalysed esterification to form acetates is considered as off-loop equilibrium as the direct conversion of acetates without hydrolysis to the alcohol

has not been observed and, to the best of our knowledge, it is not known in the literature.

### 2.3 Alcohols as substrates

Based on the reaction network and the investigations so far, other substrate alcohols and their behaviour in the reaction were investigated. For some alkyl alcohols ( $\text{C}_2$  to  $\text{C}_6$ ), it was possible to reach yields from 45% to 80% (Table 3). Conversions were always complete with side products and intermediates being formed. The main side products in all cases are the corresponding alkane and *n*-acetate esters. Methanol resulted in the lowest yield of carboxylic acid among the tested alcohols (entry 1, Table 3). A higher amount of





**Scheme 2** Reaction network of primary alcohols to carboxylic acid mainly *via* the iodides (blue top path) or the secondary alcohols mainly *via* the olefins (yellow bottom path) with CO from the rWGS (green, centre).

**Table 3** Scope of the reaction: different primary and secondary alcohols were tested

Entry	Substrate	Products	Yield (%)	Ratio 1 : 2 : 3
1 <sup>a</sup>	H <sub>3</sub> C-OH		19	19
2			80	80
3			45	33 : 12
4			65	44 : 21
5			64	42 : 17 : 5
6			30	21 : 9
7			77	50 : 27
8			66	43 : 18 : 5
9			72	72
10 <sup>b</sup>			44	44
11			80	80

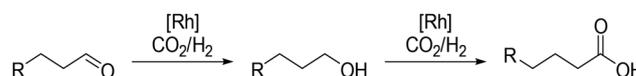
Reaction conditions: 1.88 mmol substrate, 46 μmol [RhCl(CO)<sub>2</sub>]<sub>2</sub>, 1 ml acetic acid (primary alcohols) or 2 ml acetic acid (secondary alcohols), 3.5 mol mol<sub>Rh</sub><sup>-1</sup> *p*-TsOH·H<sub>2</sub>O (secondary alcohols), 2.5 mol mol<sub>Rh</sub><sup>-1</sup> CHI<sub>3</sub>, 5 mol mol<sub>Rh</sub><sup>-1</sup> PPh<sub>3</sub>, 20 bar CO<sub>2</sub>, 20 bar H<sub>2</sub> (primary alcohols) or 10 bar H<sub>2</sub> (secondary alcohols), and 160 °C. For all substrates a conversion of 99% or higher was obtained. <sup>a</sup> 1 mL propionic acid. <sup>b</sup> Conditions for secondary alcohols applied.

methane is formed as a side product compared to other substrates as it cannot form olefins and does not undergo S<sub>N</sub> reactions easily. For substrates which can form regio-isomers, the *n*-acid is consistently more abundant with a ratio of 2 : 1 compared to the iso-acid. In the case of *tert*-butanol, only one isomer is formed and no tertiary carboxylic acid is detected (Table 3, entry 10). The preferred regioselectivity for carbonylation at the less substituted carbon demonstrates that the C–C bond formation occurs in the coordination sphere of the rhodium catalyst (Keuleman's rule).<sup>51</sup> In purely acid catalysed systems for the synthesis of carboxylic acids *via* CO and H<sub>2</sub>O, the more substituted carbon is preferentially carbonylated, due to a higher stability of the corresponding carbocation intermediate (Koch–Haaf-synthesis).<sup>52</sup>

#### 2.4 Ketones and aldehydes as substrates

Next, aldehydes and ketones were considered as possible substrates as they might be expected to be hydrogenated to the corresponding primary or secondary alcohols in the presence of H<sub>2</sub>, resulting in a fully integrated tandem hydrogenation/carbonylation network using CO<sub>2</sub>/H<sub>2</sub> as the C1 building block (Scheme 3).

The reaction was investigated starting with cyclohexanone (CHN) due to its simplicity, since just one acid-product can be formed (cyclohexanecarboxylic acid, CA). The best conditions



**Scheme 3** Tandem reaction sequence of aldehydes and ketones to form carboxylic acids *via* a hydrogenation of the carbonyl group to the alcohols and subsequent carbonylation of the alcohol using CO<sub>2</sub>/H<sub>2</sub> as the reducing atmosphere and the C1 building block.



for 2-BuOH were used for the optimization of ketones because of the parallels between the two classes of substrates. Under these initial conditions, 68% of CA is formed at a conversion >99% (Table 4, entry 1). The most influential parameters ( $H_2$  pressure, volume of acetic acid and the reaction temperature) were studied as for the secondary alcohols to obtain high yields. An increase of  $H_2$  pressure from 10 to 20 bar increases the yield of carboxylic acid to 83% (Table 4, entries 1–3). A further increase up to 30 bar does not lead to any improvement, since the hydrogenolysis reaction towards cyclohexane becomes favoured. This finding agrees with the stoichiometry of the reaction as higher amounts of  $H_2$  are needed to convert the ketone into secondary alcohols before reacting to form carboxylic acids. In particular, it is reported that Rh/phosphine systems are active in the reduction of ketones to alcohols in the presence of  $H_2O$ , which acts as a promoter.<sup>53–58</sup>

Afterwards, the effects of different amounts of solvents and the temperature were investigated. The best temperature and solvent for ketones were found to be the same as for the secondary alcohols with 160 °C and 2 mL of acetic acid (Table 4, entries 2, 4–7). Under optimised conditions, a yield of 83% of cyclohexane carboxylic acid was achieved starting from cyclohexanone (details in the ESI, Table S5†). To the best of our knowledge, this yield is the highest obtained from ketones with  $CO_2$  and  $H_2$ .<sup>59</sup>

The sequential hydrogenation/carbonylation process is also reflected by the pressure drop as for example in the conversion of 2-butanone or 2-butanol to the C5 carboxylic acids (ESI, Fig. S10†). While the pressure-drop measured for 2-butanol is 7 bar, the pressure-drop for 2-butanone is 15 bar, in line with the theoretical pressure drop calculated for the ketone (details are reported in the ESI, Scheme S1†). Analysis of the reaction solution at different reaction times also clearly shows 2-butanol as an intermediate in the reaction sequence (ESI, Fig. S1†).

**Table 4** Influence of different reaction parameters on hydroxycarbonylation of cyclohexanone with  $CO_2$  and  $H_2$

Entry	Volume of acetic acid (ml)	Temperature (°C)	$H_2$ -pressure (bar)	Yield (%)
1	2	160	10	68
2	2	160	20	83
3	2	160	30	82
4	1	140	20	54
5	3	180	20	53
6	2	140	20	66
7	2	180	20	76

If not specified, conversion is over 99% and the mass balance is around or above 80%. Reaction conditions: 1.88 mmol CHN, acetic acid as solvent, 46  $\mu\text{mol}$   $[\text{RhCl}(\text{CO})_2]_2$ , 2.5 eq.  $\text{CHI}_3$ , 5 eq.  $\text{PPh}_3$ , and 20 bar  $CO_2$ .

Various ketones could be converted to the C1 elongated carboxylic acids. Conversions of the ketones were always complete and the range of by-products was independent of the substrate used (corresponding acetate, iodide, olefin and alkane) with the alkane being the main side product in all reactions. On increasing the chain length from  $C_3$  to  $C_6$  ketones, the yield increases from 35% to 75%. Interestingly, the  $\alpha,\beta$ -unsaturated ketone 2-cyclohexen-1-one led to the monocarboxylic acid also in high yield (Table 5, entry 5, 79%).

For aldehydes the conditions optimized for primary alcohols were used as the starting point. A moderate yield of 37% of the C5 carboxylic acids was obtained starting from butanal ( $n$ :iso = 2.3). Increasing the  $H_2$  pressure to 30 bar increased the yield up to 45%, reflecting the additional need for hydrogen during the reduction. While full optimization was not carried out in this case, the system clearly shows potential for the direct conversion of aldehydes to C1 elongated carboxylic acids as well.

## 2.5 Industrially relevant mixtures as substrates

As the catalytic transformation reported here allows the conversion of ketones and alcohols in the same way, it was evaluated for the transformation of mixtures to their corresponding carboxylic acids. For example, the mixture of cyclohexanol and cyclohexanone (so-called KA-Oil) is industrially produced from the oxidation of cyclohexane. Using the conditions optimized

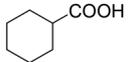
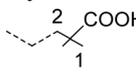
**Table 5** Scope of the reaction: different ketones were tested as substrates

Entry	Substrate	Products	Yield (%)	Ratio 1 : 2 : 3
1			35	24 : 11
2			54	37 : 17
3			75	43 : 26 : 6
4			83	83
5			79	79
6			48	48
7			38	endo: 1 exo: 37 <sup>a</sup>

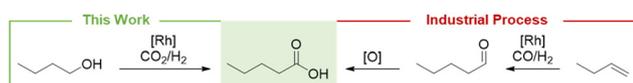
Reaction conditions: 1.88 mmol substrate, 46  $\mu\text{mol}$   $[\text{RhCl}(\text{CO})_2]_2$ , 1 ml acetic acid (primary alcohols) or 2 ml of acetic acid (secondary alcohols), 3.5 mol  $\text{mol}_{\text{Rh}}^{-1}$   $p\text{-TsOH}\cdot\text{H}_2\text{O}$  (secondary alcohols), 2.5 mol  $\text{mol}_{\text{Rh}}^{-1}$   $\text{CHI}_3$ , 5 mol  $\text{mol}_{\text{Rh}}^{-1}$   $\text{PPh}_3$ , 20 bar  $CO_2$ , 20 bar  $H_2$  (primary alcohols) or 10 bar  $H_2$  (secondary alcohols), and 160 °C. For all substrates a conversion of 99% or higher was obtained. <sup>a</sup> Determined by NMR.



**Table 6** Scope of the reaction: industrially relevant mixtures of substrates

Entry	Substrate	Products	Yield (%)	Ratio
1 <sup>a</sup>	KA oil (ketone alcohol oil)		79	79
2 <sup>b</sup>	ABE mixture (acetone–butanol–ethanol) 3 : 6 : 1		C <sub>4</sub> : 28 C <sub>5</sub> : 43 C <sub>3</sub> : 99	20 : 8 30 : 13 99

Conversions: >99%. <sup>a</sup> Cyclohexanone : cyclohexanol = 1 : 1. Reaction conditions: 1.88 mmol substrate, 46 μmol [RhCl(CO)<sub>2</sub>]<sub>2</sub>, 2 mL acetic acid, 3.5 mol mol<sup>-1</sup> *p*-TsOH·H<sub>2</sub>O, 2.5 mol mol<sup>-1</sup> CH<sub>3</sub>, 5 mol mol<sup>-1</sup> PPh<sub>3</sub>, 20 bar CO<sub>2</sub>, 20 bar H<sub>2</sub>, and 160 °C. <sup>b</sup> Reaction conditions: 1.88 mmol substrate, 46 μmol [RhCl(CO)<sub>2</sub>]<sub>2</sub>, 2 mL acetic acid, 2.5 mol mol<sup>-1</sup> CH<sub>3</sub>, 5 mol mol<sup>-1</sup> PPh<sub>3</sub>, 20 bar CO<sub>2</sub>, 20 bar H<sub>2</sub>, and 160 °C.

**Scheme 4** Production of valeric acid *via* the current industrial two-step approach based on fossil resources vs. the single step renewable approach presented in this work.

for cyclohexanol alone, cyclohexylcarboxylic acid was obtained as a product with a yield of 79% (Table 6, entry 2).

Bio-based feedstocks are also often complex mixtures, as for example acetone, butanol, and ethanol from the fermentation of carbohydrates (ABE process). Notably, the mixture obtained from ABE fermentation is transformed successfully to C<sub>3</sub> (99%), C<sub>4</sub> (28%), and C<sub>5</sub> (43% yield) carboxylic acids using the optimized conditions for primary alcohols (Table 6, entry 1). This single step transformation from renewable alcohols is particularly interesting for the platform chemical valeric acid, which is currently produced in a two-step process *via* hydroformylation and oxidation from butene obtained from fossil resources (Scheme 4).<sup>1</sup>

### 3. Conclusion

The application of CO<sub>2</sub> as a C1 building block is an important topic in green chemistry.<sup>60</sup> Carboxylic acids have many important applications, making their synthesis from CO<sub>2</sub> and intermediates of the current value chain or bio-based feedstocks such as alcohols and other oxygenated substrates highly desirable. In this work, a homogeneous catalytic system for the synthesis of carboxylic acids from alcohols, CO<sub>2</sub> and H<sub>2</sub> was developed. The carboxylic acid yield was optimized in parameter screening experiments with the highest yields obtained for secondary alcohols of 80% and for primary alcohols of 64%.

After the optimization, the reaction network was investigated in depth. The role of the individual components of the catalytic system was elucidated in detail. It was shown that the

overall transformation is a tandem process comprising the reverse water–gas–shift–reaction of CO<sub>2</sub> and H<sub>2</sub> to CO and H<sub>2</sub>O, integrated with a subsequent carbonylation step. Both steps are catalysed by organometallic rhodium complexes formed from a single precursor under the reaction conditions. The carbonylation of the alcohols occurs either *via* the olefin formed by acid-catalysed dehydration or *via* the iodoalkane formed by nucleophilic substitution. Primary alcohols follow preferentially the substitution pathway, while secondary alcohols react mainly through the olefin path.

The scope of substrates of this reaction was extended from butanols used for the mechanistic investigation to a range of primary and secondary alcohols. Furthermore, it was shown that ketones and aldehydes can be hydrogenated *in situ* to alcohols before they undergo the hydroxycarbonylation reaction. Mixtures of substrates as applied in industry were successfully used in the reaction. In particular, the ABE fermentation mixture of acetone, butanol and ethanol is very promising, as it allows the conversion of biomass-derived C2 to C4 oxygenates to value-added products in a single reaction step.

In summary, the current study substantiates the potential of CO<sub>2</sub>/H<sub>2</sub> as C1 building blocks for the general synthesis of carboxylic acids starting from alcohols, ketones, and aldehydes, and even mixtures thereof. This opens novel synthetic pathways to carboxylic acids based on renewable feedstocks as “short cuts” compared to the conventional sequence of hydroformylation and oxidation starting from fossil-based olefins.

## 4. Experimental

### 4.1 General considerations

All reactions were performed and compounds were handled under an inert gas atmosphere (Argon 4.8 Messer, Germany) if not stated otherwise, using the Schlenk technique or were handled in a glovebox (MBraun LabMaster SP).

### 4.2 Solvents and chemicals

Acetic acid and other solvents used were dried and stored over molecular sieves (4 Å) and degassed by bubbling argon through a frit for at least 1 h. All liquid substrates were degassed by at least three freeze–pump–thaw cycles and stored over molecular sieves (4 Å) under argon. Cyclohexane oxide was stored under argon and the molecular sieves used for drying were removed after 24 h. Deionized water was taken from a reverse-osmosis purification system (Werner EasyPure II) and degassed by bubbling argon with a frit for at least 1 h. The water contents of all organic solvents and substrates were measured by a Karl-Fischer titration (Metrohm 756 F Coulometer). All reagents were commercially supplied and used as received, unless stated otherwise.

### 4.3 Mass spectrometry

Mass spectroscopy measurements were performed on a Varian 1200L Quadrupole Ms/ms using the ESI ionization method.



The detected masses are given in  $m/z$  and correlated with calculated masses of the respective species.

#### 4.4 Gas chromatography

GC analyses of the liquid phases were performed on a Trace GC Ultra (Thermo Scientific) using a packed CP-WAX-52-CB column (length = 60 m, diameter = 0.25 mm) and a flame ionization detector (FID) or mass spectroscopy detector (MS). Analysis of butane and butene gases was performed on a Schromat using a capillary PLOT  $\text{Al}_2\text{O}_3$  column (length = 50 m) equipped with an FID. GC analysis of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2$  gases was performed on an HP6890 using a capillary Chem Carbon ST column (length = 2 m) and a thermal conductivity detector (TCD). Examples of the different types of chromatograms are reported in the ESI (Fig. S11–S13<sup>†</sup>).

Liquid substances were analysed using ( $\pm$ )-1-phenylethanol and/or  $n$ -dodecane as the standard. Acetone was used as a solvent for the work-up procedure (for cyclohexanol reactions acetone was substituted by dichloromethane). The correction factors were calculated preparing solutions with known amounts of substances and standard. The gaseous substances were quantified using ethane as a standard. As for the liquid samples, the correction values were obtained from self-made gas solutions with known amounts of gases.

#### 4.5 NMR analysis

NMR measurements were conducted on a Bruker AVIII-300 spectrometer (300 MHz) at ambient temperature. The  $^2\text{H}$ -NMR measurements were conducted on a Bruker AVIII HD-600 spectrometer (600 MHz) at ambient temperature. For  $^1\text{H}$ ,  $^2\text{H}$  and  $^{13}\text{C}$  chemical shifts are given in ppm relative to tetramethyl silane. For  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, chemical shifts are given in ppm relative to  $\text{H}_3\text{PO}_4$ .

#### 4.6 Autoclave reactions

The catalytic runs were performed in 10 ml stainless steel autoclaves. The autoclaves were equipped with glass inlets in which the reactions took place. The autoclaves containing iodoform ( $\text{CHI}_3$ ), triphenylphosphine ( $\text{PPh}_3$ ) and *para*-toluenesulfonic acid monohydrate ( $p\text{-TsOH}\cdot\text{H}_2\text{O}$ ) were evacuated under high vacuum for at least one hour and then charged with an argon atmosphere. Stock solutions of the catalyst precursor were prepared and transferred to the autoclave, which was then pressurized with  $\text{CO}_2$  and  $\text{H}_2$  (or  $\text{CO}$ ,  $^{13}\text{CO}$  and  $\text{D}_2$  in the labelling experiments). The mixture was heated and stirred for the desired reaction time after which the autoclave was cooled down and the pressure was relieved. The obtained reaction mixture was analysed *via* gas chromatography with a flame ionization detector (GC FID) and a mass spectroscopy detector (GC MS).

Catalytic tests were repeated two or more times. The corresponding error bars are shown in the graphs or tables or indicated in the text. Errors for side products are not indicated for simplicity reasons, but they are usually around  $\pm 2\%$ .

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 J. Kubitschke, H. Lange and H. Strutz, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2014, pp. 1–18.
- 2 M. Hoelscher, C. Guertler, W. Keim, T. E. Mueller, M. Peters and W. Leitner, *Z. für Naturforsch. B*, 2012, **67**, 961–975.
- 3 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- 4 E. A. Quadrelli, G. Centi, J. L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194–1215.
- 5 G. Centi, E. A. Quadrelli and S. Perathoner, *Energy Environ. Sci.*, 2013, **6**, 1711.
- 6 K. J. Edgar, in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc., 2002, pp. 129–158.
- 7 Z. W. Wicks, in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc., 2007.
- 8 M. Szilagyi, in *Patty's Toxicology*, John Wiley & Sons, Inc., 2012, pp. 471–532.
- 9 J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke and H. Gosselink, *Angew. Chem., Int. Ed.*, 2010, **49**, 4479–4483.
- 10 F. Röhrscheid, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2000.
- 11 H. Koch and W. Haaf, *Angew. Chem.*, 1958, **70**, 311–311.
- 12 W. Reppe and H. Kröper, *Liebigs Ann.*, 1953, **582**, 38–71.
- 13 U.-R. Samel, W. Kohler, A. O. Gamer, U. Keuser, S.-T. Yang, Y. Jin, M. Lin and Z. Wang, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2014, pp. 1–20.
- 14 A. Haynes, *Adv. Catal.*, 2010, **53**, 1–45.
- 15 T. W. Dekleva and D. Forster, *Mechanistic aspects of transition-metal-catalyzed alcohol carbonylations*, Vol. 34, 1986.
- 16 J. Hjortkjaer and J. C. Aerbo Jørgensen, *J. Mol. Catal.*, 1978, **4**, 199–203.
- 17 J. Hjortkjaer and J. C. E. Jørgensen, *J. Chem. Soc., Perkin Trans. 2*, 1978, 763–766.
- 18 S. B. Dake, D. S. Kolhe and R. V. Chaudhari, *J. Mol. Catal.*, 1984, **24**, 99–113.



- 19 B. R. Sarkar and R. V. Chaudhari, *Catal. Surv. Asia*, 2005, **9**, 193–205.
- 20 R. S. Ubale, A. A. Kelkar and R. V. Chaudhari, *J. Mol. Catal. A: Chem.*, 1997, **118**, 9–19.
- 21 C. Carlini, M. Di Girolamo, M. Marchionna, A. M. R. Galletti and G. Sbrana, *Stud. Surf. Sci. Catal.*, 1998, **119**, 491–496.
- 22 B. J. Daniel, B. P. Gracey and J. G. Sunley, WO2009077726A1, GB, 2009.
- 23 K. Matsushita, T. Komori, S. Oi and Y. Inoue, *Tetrahedron Lett.*, 1994, **35**, 5889–5890.
- 24 Q. Cao, N. L. Hughes and M. J. Muldoon, *Chemistry*, 2016, **22**, 11982–11985.
- 25 D. C. Roe, R. E. Sheridan and E. E. Bunel, *J. Am. Chem. Soc.*, 1994, **116**, 1163–1164.
- 26 E. Amadio, Z. Freixa, P. W. N. M. van Leeuwen and L. Toniolo, *Catal. Sci. Technol.*, 2015, **5**, 2856–2864.
- 27 L. Wu, X. Fang, Q. Liu, R. Jackstell, M. Beller and X.-F. Wu, *ACS Catal.*, 2014, **4**, 2977–2989.
- 28 M. Sakamoto, I. Shimizu and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1065–1078.
- 29 K. Dong, R. Sang, J. Liu, R. Razzaq, R. Franke, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, 2017, **56**, 6203–6207.
- 30 N. Tsumori, Q. Xu, Y. Souma and H. Mori, *J. Mol. Catal. A: Chem.*, 2002, **179**, 271–277.
- 31 B. R. Sarkar and R. V. Chaudhari, *Catal. Today*, 2012, **198**, 154–173.
- 32 E. Iglesia, J. G. Sunley, D. J. Law and A. Bhan, US20080146833A1, The University of California, USA; BP Chemicals Ltd. USA, 2008, p. 5.
- 33 Z. Zhang, J.-H. Ye, T. Ju, L.-L. Liao, H. Huang, Y.-Y. Gui, W.-J. Zhou and D.-G. Yu, *ACS Catal.*, 2020, **10**, 10871–10885.
- 34 Z. Fan, Y. Yi and C. Xi, *Asian J. Org. Chem.*, 2022, **11**, e202200207.
- 35 W. Leitner and J. Klankermayer, *Science*, 2015, **350**, 629–630.
- 36 X. Zhang, W.-Z. Zhang, L.-L. Shi, C.-X. Guo, L.-L. Zhang and X.-B. Lu, *Chem. Commun.*, 2012, **48**, 6292–6294.
- 37 M. Juhl, S. L. R. Laursen, Y. Huang, D. U. Nielsen, K. Daasbjerg and T. Skrydstrup, *ACS Catal.*, 2017, **7**, 1392–1396.
- 38 Y. Liu, J. Cornella and R. Martin, *J. Am. Chem. Soc.*, 2014, **136**, 11212–11215.
- 39 F. Atsushi, G. Naotaka, K. Norikazu, H. Masafumi and K. Sanshiro, *Chem. Lett.*, 1995, **24**, 567–568.
- 40 F. Juliá-Hernández, T. Moragas, J. Cornella and R. Martin, *Nature*, 2017, **545**, 84–88.
- 41 R. Martin Romo, F. Julia Hernandez and J. Cornella, *Catalytic carboxylation of activated alkanes and/or olefins with carbon dioxide*, WO2018010932A1, 2018.
- 42 A. L. Lapidus, S. D. Pirozhkov and A. A. Koryakin, *Catalytic Synthesis of propionic acid by carboxylation of ethylene with carbon dioxide*, Plenum Publishing Corporation, 1979.
- 43 H. Hoberg, Y. Peres, C. Krüger and Y.-H. Tsay, *Angew. Chem.*, 1987, **99**, 799–800.
- 44 A. Tortajada, R. Ninokata and R. Martin, *J. Am. Chem. Soc.*, 2018, **140**, 2050–2053.
- 45 T. G. Ostapowicz, M. Schmitz, M. Krystof, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Ed.*, 2013, **52**, 12119–12123.
- 46 M. Cui, Q. Qian, J. Zhang, C. Chen and B. Han, *Green Chem.*, 2017, **19**, 3558–3565.
- 47 Q. Qian, J. Zhang, M. Cui and B. Han, *Nat. Commun.*, 2016, **7**, 11481.
- 48 Y. Zhang, Y. Wang, Q. Qian, Y. Li, B. B. Asare Bediako, J. Zhang, J. Yang, Z. Li and B. Han, *Green Chem.*, 2022, **24**, 1973–1977.
- 49 J. T. Vossen, A. J. Vorholt and W. Leitner, *ACS Sustainable Chem. Eng.*, 2022, **10**, 5922–5931.
- 50 B. G. Frederick, G. Apai and T. N. Rhodin, *J. Am. Chem. Soc.*, 1987, **109**, 4797–4803.
- 51 A. I. M. Keulemans, A. Kwantes and T. van Bavel, *Recl. Trav. Chim. Pays-Bas Belg.*, 1948, **67**, 298–308.
- 52 H. Koch and W. Haaf, *Liebigs Ann.*, 1958, **618**, 251–266.
- 53 R. Noyori and O. Takeshi, *Angew. Chem., Int. Ed.*, 2001, **40**, 40–73.
- 54 Y. Chi, W. Tang and X. Zhang, in *Modern Rhodium-Catalyzed Organic Reactions*, WILEY-VCH Verlag GmbH & Co. KGaA, 2005, pp. 1–31.
- 55 M. J. Burk, T. G. P. Harper, J. R. Lee and C. Kalberg, *Tetrahedron Lett.*, 1994, **35**, 4963–4966.
- 56 R. R. Schrock and J. A. Osborn, *J. Chem. Soc. D*, 1970, 567–568.
- 57 V. Polo, R. R. Schrock and L. A. Oro, *Chem. Commun.*, 2016, **52**, 13881–13884.
- 58 P. Etayo and A. Vidal-Ferran, *Chem. Soc. Rev.*, 2013, **42**, 728–754.
- 59 Y. Zhang, J. Zhang, Y. Wang, Y. Li, J. He, Y. Wang, L. Zhang, Z. Wang, Q. Qian and B. Han, *Organometallics*, 2023, **42**, 2312–2318.
- 60 M. Poliakoff, W. Leitner and E. S. Streng, *Faraday Discuss.*, 2015, **183**, 9–17.

