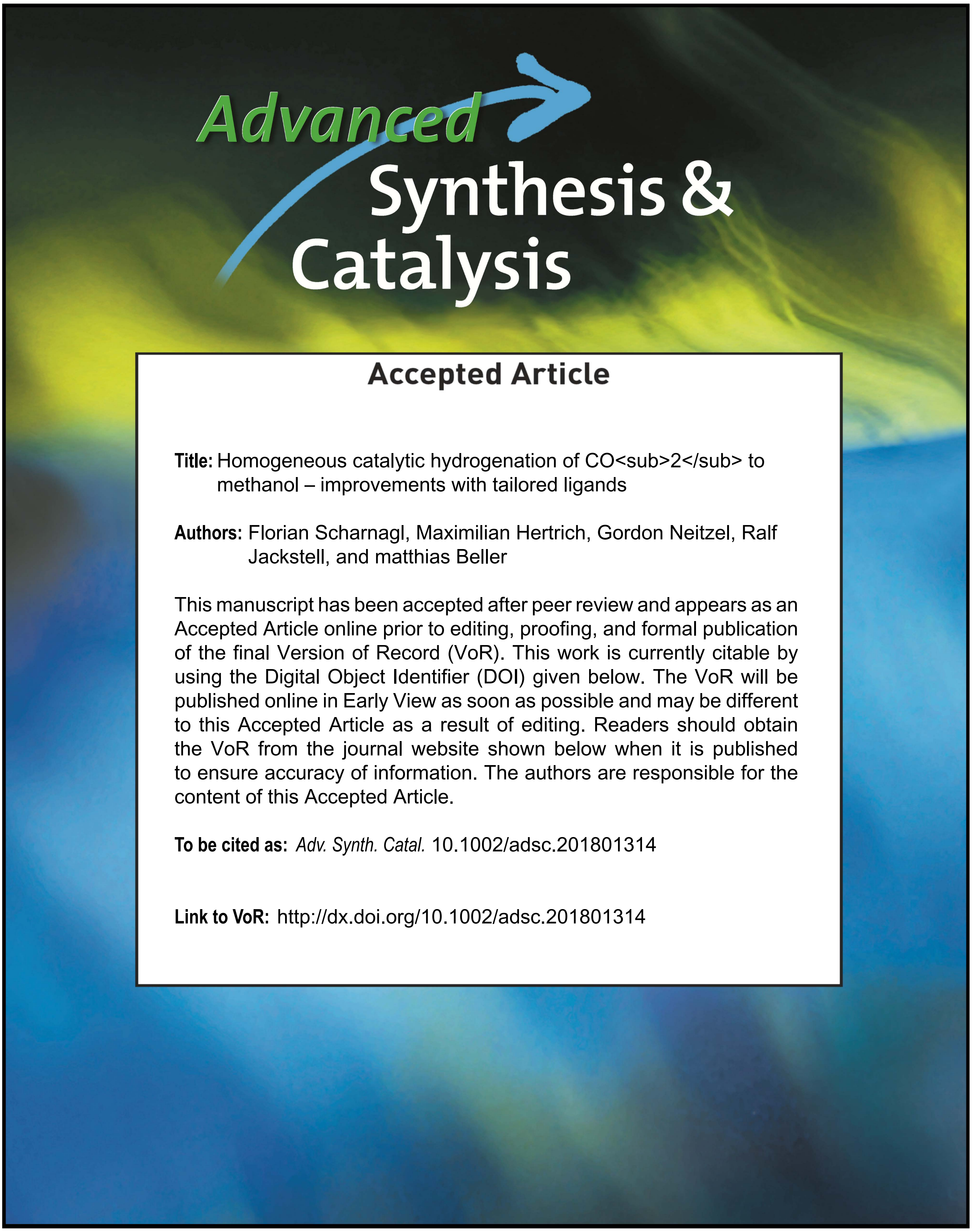

Advanced Synthesis & Catalysis

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Homogeneous catalytic hydrogenation of CO_2 to methanol – improvements with tailored ligands

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Abstract. Improved molecularly-defined cobalt catalysts for the hydrogenation of carbon dioxide to methanol have been developed. A key factor for increased productivity (up to twofold compared to previous state-of-the-art-system) is the specific nature of substituents on the triphos ligand. In addition, the effect of metal precursors, and variations of additives have been investigated.

Keywords: carbon dioxide; methanol; homogeneous catalysis; triphos; hydrogenation

Introduction

The hydrogenation of mixtures of carbon monoxide, carbon dioxide and hydrogen to methanol is one of the most important catalytic processes in the area of industrial bulk chemicals.[1] In fact, there was an annual demand of more than 90 million tons in 2016.[2] In addition to current applications, methanol is considered as potential energy carrier, within the concept of “methanol economy”, which has been proposed by Asinger[3] and Olah.[4] In this vision, either methanol or its derivative dimethylether is used for fuel cells or engines, respectively.[5]

Today, the present route to methanol uses synthesis gas as main feedstock, which is transformed with water to carbon dioxide *in situ*. The majority of these processes make use of $Cu/ZnO/Al_2O_3$ catalyst systems at 190-270 °C and 15-90 bar pressure.[6] In recent years, an increasing interest exists for methanol production directly by carbon dioxide hydrogenation.[7] As an example, besides pilot applications, the so-called “George Olah CO_2 to Renewable Methanol Plant” exists in Iceland with a capacity of about 4’000 tons per year.[8] Obviously, the particular conditions for low cost energy are crucial for this demonstration unit. For the future a sustainable methanol production on a larger scale necessitates hydrogenation of (captured) CO_2 with H_2, which in turn comes from electrolysis of water.[5b, 9] Advantageously, such a concept offers the possibility for a decentralized supply of methanol from CO_2.

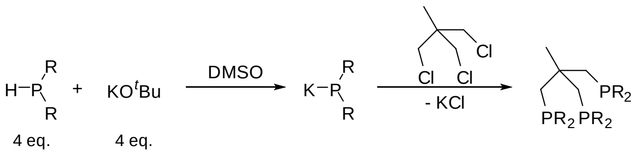
Although several heterogeneous materials are known for the direct conversion of CO_2 to methanol, similar homogeneous approaches with organometallic complexes are still at an early stage.[10] The majority of these molecularly-defined systems work under basic conditions. For instance, basic pre-activation of CO_2 with amines and subsequent hydrogenation of the intermediate to methanol in a second step was demonstrated by the groups of Milstein,[11] Sanford,[12] Olah/Prakash,[1b, 13] and Wass,[14] as well as Martins and Pombeiro.[15]

On the other hand, only few systems are known for direct CO_2 hydrogenation to methanol, which requires acidic conditions. As a step in this direction, Huff and Sanford reported a Ru-based cascade catalysis process, which involves three different catalysts at once.[16] In this system, CO_2 was hydrogenated to formic acid, which was subsequently esterificated in the presence of acid. Eventually, the ester was hydrogenated to methanol with an overall TON of 2.5. Furthermore, the CO_2 reduction to methanol at ambient, aqueous, acidic conditions was enabled by a disproportionation strategy. The groups of Himeda and Laurenczy reported Ir-based, sulfuric acid co-catalysed transformation of CO_2 to formic acid, followed by complete and selective decomposition to methanol by regenerating CO_2, again.[17]

However, all these systems involve either pre-activation of CO_2 or multiple catalysts for the formation of methanol. For a direct process, the tridentate phosphorous-ligand triphos (1,1,1-tris(diphenylphosphinomethyl)ethane) plays a crucial role. First, the groups of Klankermayer and Leitner expanded their previously published studies on the hydrogenation of carboxylic acids with a system based on this very ligand and ruthenium to the hydrogenation of CO_2.[18] Here, methanol was formed in the presence of $HNTf_2$ (bis(trifluoromethane) sulfimide) at 140 °C, 20 bar CO_2 and 60 bar H_2 with a TON of up to 221.[19] The TON was later doubled to 442 by reducing the catalyst loading by half, along with an extensive mechanistic investigation *via* NMR, MS and computational studies.[20] The group of de Bruin transferred this concept to cobalt, which was able to hydrogenate carboxylic esters and acids with high conversion at 100 °C.[21] In continuation of this work, the first homogeneous, base-metal catalyst for the direct methanol production from CO_2 was reported by our group in 2017.[22] The combination of triphos and $Co(acac)_3$ with $HNTf_2$ as an additive in a solvent mixture of THF/ethanol gave methanol with a TON of 50. The presence of ethanol was found to be important for this system, even though ethyl formate seems not to be an intermediate in this reaction. Here, we report an improved cobalt catalyst system which allows for the synthesis of methanol at low temperature (90-100°C) with improved turnover numbers and demonstrates the possibility to run such a process without additives.

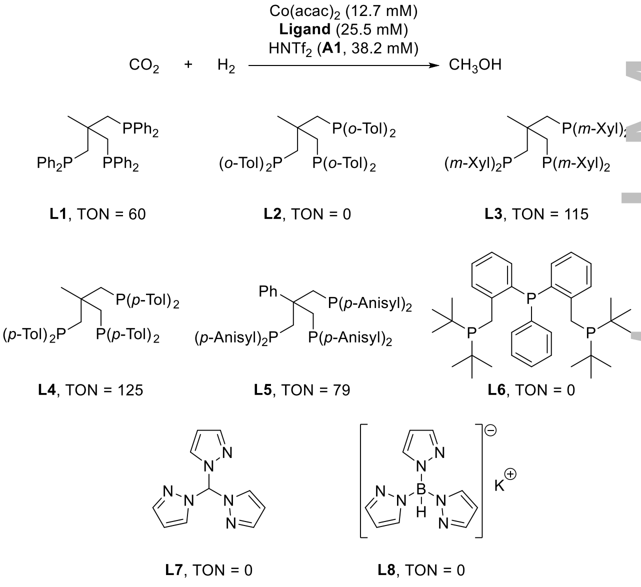
Results and Discussion

Basically all the known homogeneous catalysts for direct CO_2 to methanol conversion make use of the ligand triphos or its derivatives. In this respect, modifications of the ligand skeleton, but also variation of the phosphorus substituents are of general interest.[23] Already in 1994, Huttner and co-workers developed a convenient methodology for the preparation of aryl-modified triphos derivatives.[24] Starting from secondary phosphines and threefold chloro-substituted neopentane (1,1,1-tris(chloromethyl) ethane) in presence of potassium hydroxide a simple metathesis reaction in DMSO gave the corresponding tripod ligand, water and potassium chloride as products. Based on a slightly modified procedure,[25] we have recently reported the preparation of a small library of such ligands.[23]



Scheme 1: General synthesis of triphos-derivatives.

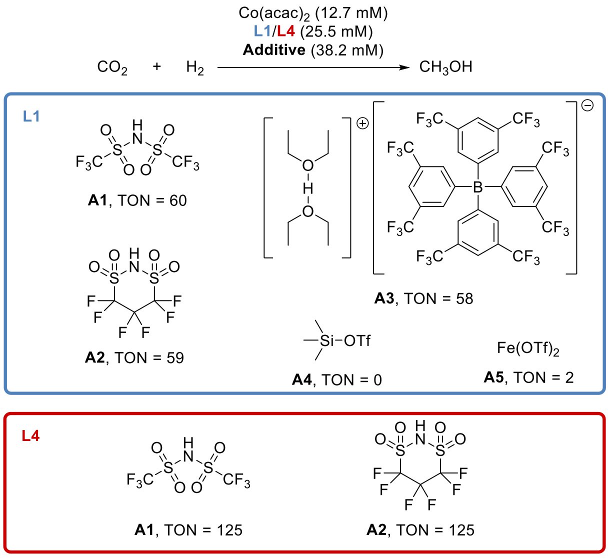
Hence, ligands **L1-L6** were tested for the CO_2-hydrogenation to methanol in the presence of cobalt salts and $HNTf_2$ as an additive. Using sublimed $Co(acac)_2$ together with the parent ligand **L1** gave a slightly more active catalyst system (TON: 60) than $Co(acac)_3$ (TON: 50). As shown in Scheme 2, using the *ortho*-substituted derivative **L2** instead of **L1** inhibited the reaction completely. This indicates the strong influence of sterically demanding groups, which likely disturb the coordination of the P-atom to the metal centre. On the other hand, methyl-substitution on the aryl substituents in *meta*- or *para*-position improved the TONs (**L3**, **L4**) by a factor of two with respect to unmodified triphos. This might have two reasons; first the electron density on phosphorus is significantly increased. Therefore, also the metal centre is electron-rich, which accelerates the H_2-activation. In addition, a substitution in *meta*- or *para*-position might prevent the formation of a μ_2-dihydrido-bridged Co-dimer. The generation of an analogous Ru-dimer was determined as deactivation pathway in the system reported by Klankermayer and Leitner.[20, 25] Unexpectedly, the stronger electron-donating methoxy-group in *para*-position (**L5**) gave a lower TON of 79.



Scheme 2: Investigation of ligands in the homogeneous hydrogenation of CO_2 to methanol with cobalt.

Reaction conditions: $Co(acac)_2$, ligand, $HNTf_2$ (1:2:3), THF:EtOH (8:3), 20 bar CO_2, 70 bar H_2, 100 °C, 24 h. Mass of methanol was determined *via* GC using hexadecane as internal standard. TON = $n_{product}/n_{catalyst}$.

Nonetheless, it is still more active than the parent triphos ligand. In addition to these ligands, few other tridentate phosphorus (**L6**) and scorpionate-type nitrogen (**L7**, **L8**) containing ligands were investigated. However, no product formation was observed for any of these ligands, which highlights the importance of the triphos-scaffold, again. Apart from the ligand, also non-coordinating acidic additives, e.g. $HNTf_2$ (**A1**) were found to be essential for hydrogenation to methanol, previously.[22a] It was hypothesised that this additive acts as a weakly coordinating counter-anion to stabilise the cationic catalytically active species. Also the group of de Bruin found that non-coordinating anions are crucial for their cobalt/triphos-based system.[21] To further investigate this effect, additional additives were tested (Scheme 3). While TMSOTf (**A4**) and $Fe(OTf)_2$ (**A5**) hardly showed any activity, Brookhart's acid (**A3**) and the cyclic triflimide **A2** gave comparable results as **A1**. These results demonstrate the importance of the additive and besides highlights that the presence of nitrogen is not mandatory for catalytic activity. Notably, also acidity seems not to be decisive, as **A2** (pK_a: -13.1 in DCE) is about 10-fold more acidic than **A1** (pK_a: -11.9 in DCE).[26]



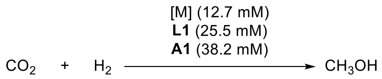
Scheme 3: Investigation of additives in the homogeneous hydrogenation of CO_2 to methanol with cobalt.

Reaction conditions: $Co(acac)_2$, ligand, $HNTf_2$ (1:2:3), THF:EtOH (8:3), 20 bar CO_2, 70 bar H_2, 100 °C, 24 h. Mass of methanol was determined *via* GC using hexadecane as internal standard. TON = $n_{product}/n_{catalyst}$.

Apart from ligands and additives, also different metals (e.g. Fe, Mn, Cu, Ni) and cobalt-precursors have been investigated for the title reaction (Table 1). Unfortunately, none of the other *3d*-metal acetylacetonate-complexes tested showed significant activity in this system. However, it was found that $Co(acac)_2$ can be replaced by either $CoCO_3$ or $Co(NTf_2)_2$. In addition, the latter precursor is also active in the absence of any additive.

Interestingly, when either an aged or refluxed (10 minutes) stock-solution of $Co(NTf_2)_2$ and **L1** in THF was used, an increased productivity (TON: 45-46) could be observed compared to a freshly prepared catalyst-solution (TON: 33). Noteworthy, a TON of 33 was also observed for the refluxed catalyst-solution already at 90 °C. Notably, the previous system based on $Co(acac)_3$ did not show any activity below 100 °C. Possibly the necessary cleavage of the ligand affords higher temperatures, and as this step is not needed in the case of $Co(NTf_2)_2$, it is active at even lower temperatures. In addition, the simplified system is still active after 67 h, as was shown *via* detection of pressure consumption (see SI). Contrary to our previous additive-containing system, a ligand to metal ratio of 1:1 gives an increased TON of 70.

Table 1: Investigation of metals and metal-precursors on the homogeneous hydrogenation of CO_2 to methanol.

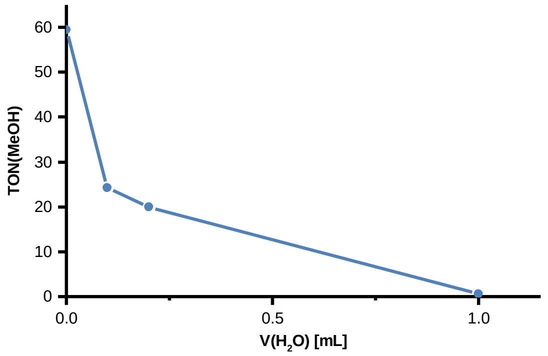


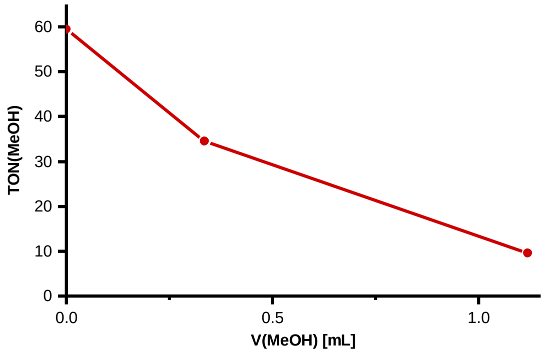
entry	metal precursor	TON (MeOH)
1	$Mn(acac)_2$	0
2	$Fe(acac)_3$	traces
3	$Ni(acac)_2$	traces
4	$Cu(acac)_2$	traces
5	$CoCO_3$	43
6	$Co_2(CO)_8$	0
7[a]	$Co(NTf_2)_2$	52
8[b]	$Co(NTf_2)_2$	45
9[b,c]	$Co(NTf_2)_2$	33
10[b,d]	$Co(NTf_2)_2$	70

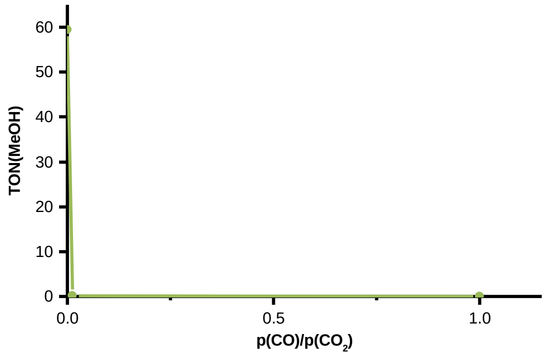
Reaction conditions: [M], ligand, $HNTf_2$ (1:2:3), THF:EtOH (8:3), 20 bar CO_2, 70 bar H_2, 100 °C, 24 h. Mass of methanol was determined *via* GC using hexadecane as internal standard. TON = $n_{product}/n_{catalyst}$. [a] 1.0 eq. of **A1** was used. [b] No additive was used. [c] Reaction was carried out at 90 °C. [d] 1.0 eq. of **L1** was used.

All these further investigations underline that the formation and stabilisation of the supposed catalytic active species $[Co(Triphos)(L)_n]^{m+}$ is required for this system. Clearly, only if the combination of metal-precursor, ligand and additive enables this formation, catalytic activity can be observed. For instance the strong Brønsted-acids **A1**, **A2**, and **A3** can potentially protonate the acetylacetonate-ligands of $Co(acac)_2$. The resulting free coordination sites of cobalt can rapidly be occupied by triphos. The conjugated base of the additive acts as weakly coordinating anion and stabilizes the cationic species. In the case of $CoCO_3$, carbon dioxide is released in strong acidic media and again cobalt can be ligated and form a cationic species. $Co(NTf_2)_2$ does not need an additive, as Tf_2N^- is weakly coordinating and triphos can therefore easily coordinate to cobalt to give $[Co(Triphos)(L)_n]^{m+}$, again.

Previously, it was shown that the activity of the cobalt-based system decreases during time.[22a] For this reason, studies on the deactivation of the catalyst in the presence of potential poisons have been conducted (Scheme 4). It was found that both products of the reaction, water and methanol, inhibit the catalyst system. With increasing amounts of them, the TON for the production of methanol decreased to a TON of 10 (1.1 ml MeOH) or 1 (1 ml of water), respectively. Hence, we tried to remove the *in-situ* produced water by addition of triethyl orthoester. Unfortunately, with a TON of 52 the catalyst performance could not be improved. Besides of product-inhibition, a major poisoning effect has carbon monoxide. Even traces of CO (CO_2:CO = 80:1) quenched the reaction completely and no methanol was detected. Hence, it is clear that catalyst improvements in the future need to take these points into account, for instance by removing the products from the product phase.







Scheme 4: Investigations on the deactivation of the catalyst in the presence of potential poisons: water (blue), methanol (red) and CO (green).

Conclusion

In conclusion, the performance of the cobalt-catalysed reduction of CO_2 to methanol has been improved. Using modified triphos ligands led to higher TON up to 125 and by replacing $Co(acac)_2$ with $Co(NTf_2)_2$, an additive free system was developed, which is also active below 100 °C. Apart, the role of the additive as a weakly coordinating anion was highlighted and catalyst deactivation pathways were identified. For further optimisations, CO-, methanol- and water-resistant catalyst systems have to be developed. Currently, further mechanistic investigations are ongoing in our laboratory, which should shed more light on this interesting topic.

Experimental Section

All chemicals were purchased from commercial sources and were used as received without additional purification, if not stated otherwise. Gases were purchased by *Linde*. All experiments were carried out under argon atmosphere by using a glovebox or standard Schlenk-techniques, unless stated otherwise. Solvents were stored over molecular sieves 4Å. THF was dried over sodium and benzophenone. Ethanol was dried over magnesium. The ligands **L2**,[27] **L3**,[25] **L4**,[25] **L5**[23] and **L6**[28] were synthesised according to reported procedures. Catalytic experiments were conducted in high pressure Parr autoclaves and stirred either mechanically, or with a cross-shaped stirring bar. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on Bruker AV-300, Bruker Fourier 300 or Bruker AV-400 spectrometers. Chemicals shifts (δ) are reported in ppm downfield of tetramethylsilane. The NMR chemical shifts are reported relative to the centre of solvent resonance [CD_2Cl_2: 5.32 (^1H), 53.8 (^{13}C), $CDCl_3$: 7.26 (^1H), 77.0 (^{13}C)]. Gas chromatography

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analysis was performed on an *Agilent* HP-6890 chromatograph with a FID detector and an *Agilent* HP Ultra 1 column (19091A-105, 50 m, 0.20 mm i.d., 0.33 µm film thickness, 100% dimethylpolysiloxane) using hydrogen as carrier gas.

Synthesis of Brookhart's acid

According to a modified literature procedure of Brookhart *et al.*[29] 1.14 mmol (1012.6 mg) Na[BAr$^F_4$] were dissolved in 14 mL Et_2O at -78 °C. To the pale yellow solution, 4.57 mL of a 1M solution of HCl in Et_2O were added. A white solid precipitated out and after 2 h stirring, the cold suspension was filtered. The filtrate was concentrated to give a white solid in a pale yellow liquid. The mixture was stored overnight and then the mother liquor was removed with a syringe. The white product was dried in high vacuum (801 mg, 69%)

General Procedure for the Hydrogenation of CO_2

Experiments in a 100 mL autoclave

0.14 mmol of metal-precursor and 0.28 mmol ligand were weighed in a Schlenk-tube inside the glovebox. In a separate Schlenk-tube were weighed in 0.42 mmol of additive, if used, inside the glovebox. Outside, the metal-precursor and the ligand were dissolved in 8 mL THF. The additive was dissolved in 3 mL ethanol. The solutions were combined and stirred for further 5-10 minutes. A 100 mL (Hastelloy® C) autoclave was sealed, and evacuated and purged with argon for three times. If a stainless-steel autoclave was used, the reaction was carried out in a glass insert. Afterwards, the catalyst-solution was injected. The autoclave was loaded with 20 bar CO_2 at room temperature, followed by 70 bar H_2. It was heated by an aluminum-block for 24 h. Finally, it was cooled with an ice-bath to quench the reaction. 20 µL hexadecane were added as internal standard and after proper stirring of the solution it was analysed by GC.

Experiments in a 25 mL autoclave

0.035 mmol of metal-precursor and 0.07 mmol ligand were weighed in a Schlenk-tube inside the glovebox. In a separate Schlenk-tube were weighed in 0.105 mmol of additive, if used, inside the glovebox. Outside, the metal-precursor and the ligand were dissolved in 2 mL THF. The additive was dissolved in 0.75 mL ethanol. The solutions were combined and stirred for further 5-10 minutes. A 25 mL Hastelloy® C autoclave was sealed, and evacuated and purged with argon for three times. Afterwards, the catalyst-solution was injected. The autoclave was loaded with 20 bar CO_2 at room temperature, followed by 70 bar H_2. It was heated by an aluminium-block for 24 h. Finally, it was cooled with an ice-bath to quench the reaction. 20 µL hexadecane were added as internal standard and after proper stirring of the solution it was analysed by GC.

Experiments with a stock-solution

0.7 mmol (433.46 mg, 1.0 eq) $Co(NTf_2)_2$ and 1.4 mmol (874.54 mg, 2.0 eq) **L1** were weighed in a 100 mL Schleck-flask inside the glovebox. Outside, 40 mL THF were added and the reddish solution was refluxed for 10 minutes, during which the colour changed to dark red/brownish (see SI). Alternatively, the fresh stock-solution was stored at room-temperature for several days, during which the same colour-change took place. For the catalytic testing, 8 mL of the stock-solution was injected in the autoclave under argon, followed by 3 mL ethanol. The autoclave was loaded with 20 bar CO_2 at room temperature, followed by 70 bar H_2. It was heated by an aluminium-block for 24 h. Finally, it was cooled with an ice-bath to quench the reaction. 20 µL hexadecane were added as internal standard and after proper stirring of the solution it was analysed by GC.

Deactivation studies for the CO_2 hydrogenation

Inhibition with water or methanol

The catalyst-solution was prepared as usual, but the indicated amounts of water or methanol, respectively, were added additionally. The reaction was then carried out and worked up as stated above.

Poisoning with CO

The catalyst-solution was prepared as usual and injected in the autoclave. For a 1:1 mixture of CO_2 and CO, the autoclave was first loaded with 10 bar CO, followed by 10 bar CO_2. Afterwards H_2 was introduced and the reaction was then carried out and worked up as stated above. For a poisoning with 1.25 vol% CO, the autoclave was first loaded with 1 atm of CO. Then, CO_2 was loaded to a total pressure of 40 bars at room temperature. The pressure was released to 10 bar, and CO_2 was loaded to a total pressure of 20 bars. Afterwards, a total pressure of 90 bar was adjusted with H_2 and the reaction was carried out and worked up as stated above.

Acknowledgements

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UPDATE

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