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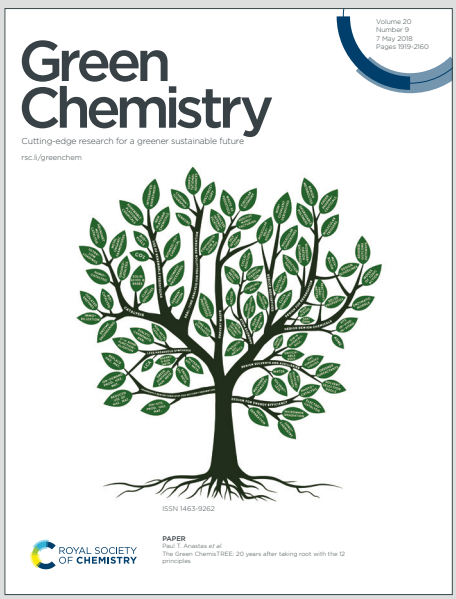

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ARTICLE

Transfer Hydrogenation of Cyclic Carbonates and Polycarbonate to Methanol and Diols by Iron Pincer Catalysts

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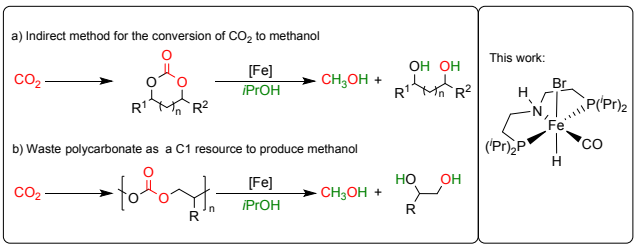
Herein, we report the first example on the use of an earth-abundant metal complex as catalyst for the transfer hydrogenation of cyclic carbonates to methanol and diols. The advantage of this method is the use of isopropanol as hydrogen source, thus avoiding the handling of flammable hydrogen under high pressure. The reaction offers an indirect route for the reduction of CO_2 to methanol. In addition, poly(propylene carbonate) was converted to methanol and propylene glycol. This methodology can be considered as an attractive opportunity for the chemical recycling of polycarbonates.

Introduction

Carbon dioxide (CO_2) is an economic, renewable and safe C1-building block for the production of organic chemicals and materials.[1-5] The conversion of this thermodynamically stable molecule into value-added products is challenging but at the same time creates the opportunity to develop new concepts and catalysts. Methanol is one of the most versatile and largest chemical commodities with a global demand of >70 million metric tons in 2015.[6] Currently, methanol is produced from syngas which is obtained mainly from natural gas and other fossil resources.[7] Methanol is an indispensable precursor for various industrial products and bulk chemicals such as acetic acid, formaldehyde, gasoline (via methanol-to-gasoline) and olefins which are produced by methanol-to-olefins (MTO) and methanol-to-propene (MTP).[8, 9] Furthermore, methanol has attracted significant attention as a liquid fuel, energy carrier in methanol fuel cells as well as hydrogen-storage material (12.5 wt% H_2). Olah recently introduced the concept of the "methanol economy" where methanol is the main carbon feedstock and energy carrier.[10, 11]

For these reasons, the reduction of CO_2 to methanol is of particular interest. Heterogeneous catalysts for the direct reduction of CO_2 with hydrogen were extensively studied and numerous active systems have been reported.[12, 13] However, most of them require high reaction temperatures (>200°C) and high hydrogen pressure. Homogeneous catalysts are potentially more active and energy efficient but often require the use of additives.[14-16] Recently, great advances have been made in the field of direct hydrogenation of CO_2 to methanol with seminal contributions from the groups of Sanford,[17] Prakash and Olah[18, 19] Klankermayer and Leitner[20, 21] employing noble metal catalysts based on ruthenium.



Scheme 1. Iron-based catalysts for transfer hydrogenation of organic carbonates.

So far, only a few examples on the use of non-noble metal catalysts were reported, e.g. Beller and coworker employed a cobalt catalyst[22] for the direct reduction of CO_2 while the group of Prakash reported a manganese-based[23] system. The latter described a sequential process for the reduction of CO_2 to methanol via pre-formed formamide reaching TONs up to 36. Notably, Milstein and co-workers were the first introduced the concept of indirect CO_2-reduction as an alternative route to methanol.[24] They used Ru pincer-type complexes of the general structure [(PNN)Ru(CO)(H)] for the catalytic hydrogenation, e.g. of dimethyl carbonate to methanol under mild conditions. The group of Ding reported the use of the Ru-MACHO pincer catalyst for the reduction of cyclic carbonates, e.g. ethylene carbonate.[25] This would in principle allow the selective production of ethylene glycol and methanol from CO_2 and ethylene oxide via ethylene carbonate in a modified Shell "OMEGA process".[26] The replacement of noble-metal catalysts by earth-abundant substitutes is also of particular interest for the indirect CO_2-reduction. Most recently three independent parallel studies by the groups of Milstein,[27] Leitner[28] and Rueping[29] on the hydrogenation of organic carbonates to methanol using manganese pincer-type complexes as catalysts

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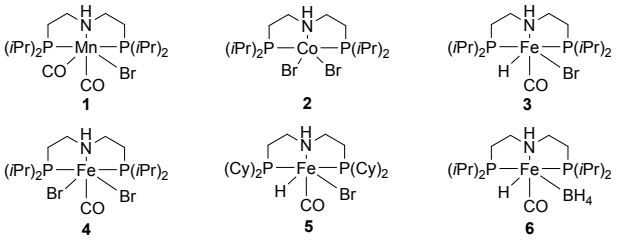
were reported. However, high pressures of highly flammable hydrogen gas and/or high temperatures were required in the above mentioned protocols.

In general, transfer hydrogenations using hydrogen donors such as readily available and non-toxic isopropanol are attractive alternatives to classical hydrogenation reactions.[30-32] These protocols are usually operational simple, avoiding the use of molecular hydrogen and expensive high pressure reactors. Notably, so far the only example of a transfer hydrogenation of cyclic carbonates to methanol and diols was reported by Hong and co-workers using a ruthenium catalyst.[33] Although the transfer hydrogenation of esters is known,[34-36] to the best of our knowledge there is no report on the transfer hydrogenation of organic carbonates by homogeneous catalysts based on earth abundant metals. The synthesis of cyclic carbonates from CO_2 and epoxides is a 100% atom economical reaction and can be performed even at room temperature and 1 atm CO_2.[37, 38] Previously, we described efficient catalytic systems based on organo- and earth-abundant metal catalysts for this reaction.[39, 40] Herein, we report the first example of the transfer hydrogenation of cyclic carbonates as well as poly carbonates to methanol and diols using iron pincer-type catalysts (Scheme 1).

Results and discussion

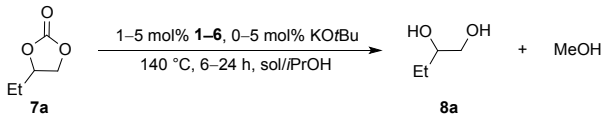
We started our investigations with three PNP pincer-type complexes **1–3** based on Fe, Mn and Co (Scheme 2).



Scheme 2. Base metal PNP pincer-type complexes 1–6 used in this study.

In preliminary experiments, 2-butylene carbonate (**7a**) was selected as a benchmark substrate for the transfer hydrogenation in the presence of catalysts **1–3** (Table 1). The reaction was conducted during 6 h with 5 mol% of catalyst in the presence of KO*t*Bu (5 mol%) using *i*PrOH as hydrogen source at 140 °C. Compared to the Mn- and Co-PNP pincer-type complexes **1** and **2** the Fe-complex **3** was found to be the most efficient catalyst for the transfer hydrogenation of carbonate **7a** (entries 1 and 2 vs. 3). Notably, this is the first example of the use of iron pincer catalysts for the reduction of cyclic carbonates. Next, complexes **4–6** were also prepared and tested. In the presence of catalyst **4** the formation of **8a** and MeOH was not observed; instead 2-hydroxybutyl isopropyl carbonate and diisopropyl carbonate were obtained (Entry 4). In contrast, use of catalysts **5** and **6** gave **8a** and MeOH although in disappointing yields under the same reaction conditions (Entries 5 and 6). Catalyst **6** is a well-known base-free pincer-type complex.[41] However, in the absence of base even lower yields were achieved (Entry 7). If no catalyst is employed some background reaction is observed under basic conditions leading to 16% **8a** and 11% diisopropyl carbonate (see SI, Scheme S1). However, in this case the formation of MeOH is not observed. It has to be mentioned that iron complex **3** had only low catalytic activity for the reduction of diisopropyl carbonate, indicating that the latter is not likely an intermediate in the catalytic cycle (see SI, Scheme S2). Typically, diisopropyl carbonate was observed as by-product which is formed from the cyclic carbonate **7a** by transesterification with *i*PrOH in the above mentioned reactions. This explains the reduced methanol yield, which is in some cases significantly lower than expected when only *i*PrOH was used as the solvent (Table 1, entries 1–6).

Table 1 Transfer hydrogenation of cyclic carbonate **7a** in the presence of base metal PNP pincer-type complexes (**1-6**).[a]



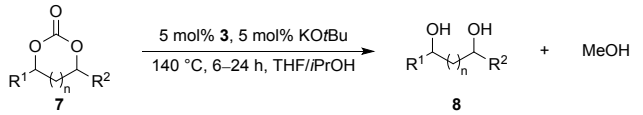
Entry	Cat.	KO*t*Bu/ mol%	Solvent	Conv. / %	Yield **8a**/ %[b]	Yield MeOH/ %[b]
1	**1**	5.0	*i*PrOH	18	11	14
2	**2**	5.0	*i*PrOH	66	51	37
3	**3**	5.0	*i*PrOH	81	80	60
4	**4**	5.0	*i*PrOH	34	-	-
5	**5**	5.0	*i*PrOH	57	55	29
6	**6**	5.0	*i*PrOH	72	63	41
7	**6**	-	*i*PrOH	52	51	22
8	**3**	5.0	THF/*i*PrOH	99	95	91
9	**3**	-	THF/*i*PrOH	37	-[c]	-
10	**3**	10	THF/*i*PrOH	99	92	34
11[d]	**3**	2.5	THF/*i*PrOH	85	81	76
12[e]	**3**	1.0	THF/*i*PrOH	56	52	36
13[f]	**3**	5.0	THF/*i*PrOH	52	47	35
14	**3**	5.0	THF/E*t*OH	99	91	59

[a] Reaction conditions: Catalyst **1–6** (5 mol%), KO*t*Bu (5 mol%), **7a** (1.0 mmol), THF (0 or 1.0 mL), *i*PrOH (4 mL), 140 °C, 6 h. [b] Determined by GC using mesitylene as the internal standard. [c] 2-hydroxybutyl isopropyl carbonate was observed as the product. [d] 2.5 mol% of catalyst **3** was used. [e] 1.0 mol% of catalyst **3** was used. [f] K_2CO_3 was used as base instead of KO*t*Bu, 24 h reaction time.

To increase the solubility of the catalyst precursor and facilitate complete deprotonation several solvents were tested (see SI, Table S1). In the presence of THF as co-solvent the transfer hydrogenation of **7a** using catalyst **3** led to diol **8a** and MeOH in excellent yields of 95% and 91% respectively (Entry 8). In the absence of base only the formation of 2-hydroxybutyl isopropyl carbonate was observed as the only product at a moderate conversion (37%) of **7a** (Entry 9). In contrast, an increase of the base loading to 10 mol% led to full conversion, but a low MeOH yield (34%) was obtained (Entry 10). In this case we observed the formation of diisopropyl carbonate as byproduct. When the catalyst loading was reduced to 2.5 mol% of **3** a reaction time of 24 h was

necessary to achieve 85% conversion of **7a** (Entry 11). Even at 1 mol% catalyst loading moderate yields of **8a (**52%) and MeOH (36%) were still achieved (Entry 12). A study on the impact of the reaction temperature revealed that 140°C was the optimal temperature (see SI, Table S2). Hong and coworkers reported the use of Ru-PNP complexes in combination with K_2CO_3 as base.[33] In our hands K_2CO_3 proved to be less effective in combination with catalyst **3** compared to KO*t*Bu (Entry 13). Recently, we reported ethanol as an efficient renewable hydrogen source for the transfer hydrogenation reaction of esters.[36] However, the conversion of cyclic carbonate **7a** with ethanol as hydrogen donor gave only moderate yields of the desired products (Entry 14).

Table 2. Substrate scope for the transfer hydrogenation of cyclic carbonates **7** in the presence of iron pincer catalyst **3**.[a]



7 8

Entry	Substrate	*t*/ h	Yield **8**/ %[b]	Yield MeOH/ %[c]
1	**7a**	6	95[c]	91
2[d]		18	72, 87[c]	83
3	**7b**	6	97[c]	92
4[e]		12	53[c]	35
5	**7c**	6	91	90
6	**7d**	12	81	73
7	**7e**	24	84	77
8	**7f**	24	83	71
9	**7g**	12	85	82
10	**7h**	24	71	62
11	**7i**	24	86	78
12	**7j**	12	92	86
13	**7k**	24	51[c]	39

[a] Reaction conditions: Catalyst **3** (5 mol%), KO*t*Bu (5 mol%), **7** (1.0 mmol), THF (1 mL), *i*PrOH (4 mL), 140 °C, 6–24 h. [b] Yield of the isolated product. [c] Determined by GC using mesitylene as the internal standard. [d] 10 mmol of **7b** was used. [e] 100 °C.

To demonstrate the potential of this new catalytic system, a variety of cyclic carbonates **7a**-**7k** were tested under the optimized conditions using iron complex **3** as transfer hydrogenation catalyst (Table 2). Ethylene carbonate (**7b**) as well as various substituted carbonates were efficiently reduced to MeOH and diols (Entries 1–10). Yields up to 97% were obtained, even though in some cases the reaction time had to be extended to achieve conversions >90%. Notably, the amount of MeOH obtained in all reactions is as expected in the range of the corresponding amounts of **8**. This indicates that reduction of the carbonate is indeed in operation rather than formation of **8** by transesterification. Significantly, the reaction can be scaled up to multi-gram quantities; e.g. ethylene carbonate (**7a**, 10 mmol) was converted to afford **8a** in 87% and methanol in 83% yield (Entry 2). We also investigated the synthesis of diol **8a** and MeOH in a one pot two step reaction sequence from butylene oxide and CO_2 (see SI for details). In the first step we used a bifunctional phosphonium salt previously developed in our group to prepare **7a**.[42, 43] The carbonate was subsequently converted in the presence of catalyst **3** to yield diol **8a** (59%) and MeOH in 59% and 47 yield, respectively. Additionally, we investigated the possibility of catalyst recycling in the conversion of **7a** to **8a** and MeOH (see SI, Figure S1). Even though the catalyst could be separated from the reaction products and reused, the yields on **8a** and MeOH dropped already significantly in the second run.

Other simple carbonates **7b**–**7f** could be converted to **8b**–**8f** in good to excellent yields (Entries 3–8). Interestingly, the double bonds in substrates **7g** and **7h** are unaffected under the reaction conditions and the unsaturated diols **8g** and **8h** were obtained in yields of 85% and 71% respectively. The disubstituted carbonate **7i** as well as the internal disubstituted substrate **7j** were converted and excellent yields of the diols and MeOH were achieved (Entries 11 and 12). The six-membered carbonate **7k** was also reduced but only a moderate conversion was observed after 24 h (Entry 13).

Subsequently, we identified and monitored the reaction intermediates produced in the transfer hydrogenation of 2-butylene carbonate (**7a**) to elucidate the possible reaction pathways using the PNP pincer-type Fe (II) catalyst **3** (See SI, for details). We only observed the presence of isopropyl formate (**11**) as intermediate. Notably, as mentioned above, in the absence of base the formation of 2-hydroxybutyl isopropyl carbonate was observed (Table 1, Entry 9). This is in agreement with the excellent study of Hong and coworkers who observed the formation of 2-hydroxyethyl isopropyl carbonate and **11** in the Ru-catalyzed transfer hydrogenation of **7b**.[33]

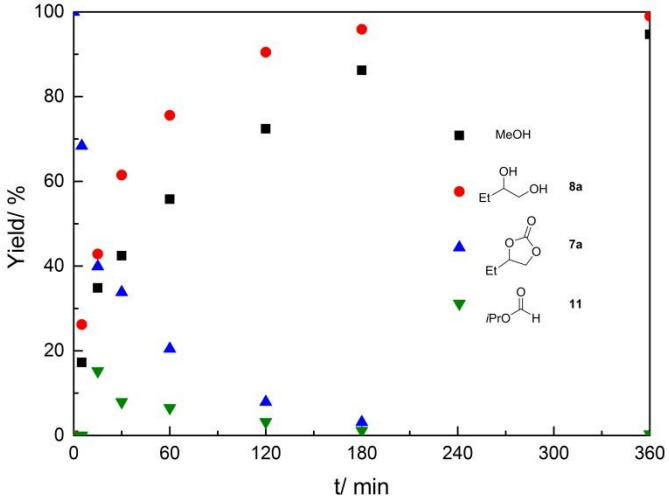
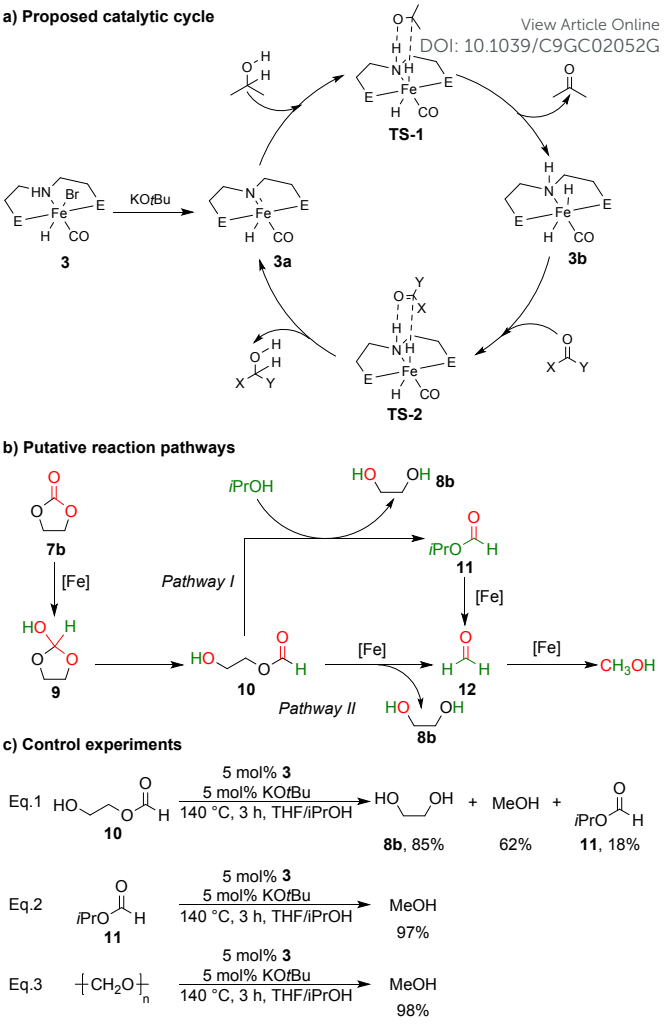


Figure 1. Reaction profile of the transfer hydrogenation of cyclic carbonate **7a**. Yields were determined by GC using mesitylene as the internal standard.

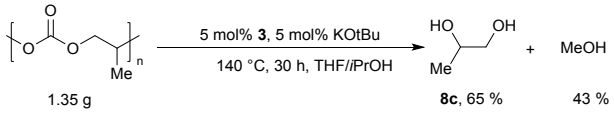
Based on these results a putative catalytic cycle and reaction pathway shown in Scheme 3 are proposed. Initially, complex **3** is deprotonated to afford the 16e complex **3a**. Subsequently, the dehydrogenation of *i*PrOH leads to the 18e complex **3b** and acetone via **TS-1** (Scheme 3a). Finally, hydrogen transfer from complex **3b** to the C=O group of a carbonyl substrate e.g. a carbonate via **TS-2** regenerates **3a** under liberation of the reduced carbonyl species. The reduction of **7b** to MeOH can proceed via two possible pathways (Scheme 3b). The initial reduction of **7b** leads to intermediate **9** which rearranges to formate **10**. The formation of formates like **10** was proposed by Leitner and coworkers as an intermediate in the hydrogenation reactions even though it was not observed by us.[28] However, the presence of **11** indicates that **10** might be formed in low concentrations and is directly transesterified to **11** under liberation of diol **8b**. In turn **11** is reduced to formaldehyde **12** which is a frequently observed intermediate in this type of reactions[33] which is than further reduced to MeOH. A second possible pathway which cannot be excluded and is often proposed for the hydrogenation of cyclic carbonates using pincer catalysts[27-29] is the reduction of **7b** to **12** via **10**.



Scheme 3. Putative reaction pathway and control experiments.

To probe this proposal we studied the conversion of **10** under our transfer hydrogenation conditions using catalyst **3** (Scheme 3c, Eq. 1). Notably, beside the final products **8b** and MeOH which were obtained in 85% and 62% yield, respectively, the reaction intermediate **11** was observed in 18% yield. Additionally, we could prove that **11** can be completely converted under our standard reaction conditions giving MeOH in 97% yield (Eq. 2). Also formaldehyde (**12**), obtained from the depolymerization of paraformaldehyde at high temperatures, was reduced in the presence of **3,** as proposed, leading to MeOH in an excellent yield of 98% (Eq. 3). The production of polycarbonate is one the most successful processes for the conversion of CO_2 into value-added products, which is even performed on industrial scale.[1] Due to environmental concerns, the chemical recycling of waste polymers e.g. polycarbonate into valuable chemicals is becoming a hot topic in the field of catalysis.[44] To the best of our knowledge, there are no examples known of depolymerisation of polycarbonates by transfer hydrogenation. We envisioned **3** to be a suitable catalyst for this reaction. Thus, we converted commercially available poly(propylene carbonate) ($M_n \approx 50 \cdot 10^3$ g·mol^{-1}) in the

presence of catalyst **3** (Scheme 4). Under the optimized reaction conditions we obtained propylene glycol and MeOH in 65% and 43% yield, respectively. Notably, the formation of MeOH and diols was not detected when the well-known complex **6** was used under base-free conditions (see SI, Scheme S4). We investigated if the base (KO*t*Bu) had an additional role beside the deprotonation of **3** to form the catalytically active species **3a** (Scheme 3a). Notably, in the absences of **3** we observed the depolymerisation of the poly(propylene carbonate) under our reaction conditions in the presence of catalytic amounts (5 mol%) KO*t*Bu. The respective cyclic carbonate **7c** and diol **8c** were identified as products in the ^{1}H NMR of the reaction mixture (see SI). The latter might be formed by transesterification e.g. of **7c** with *i*PrOH. Thus, it can not be ruled out that also under the reaction conditions free base affects the polymers structure, namely leads to partial depolymerisation, which in turn facilitates the transfer hydrogenation of lower molecular weight fragments.



Scheme 4. First example on the transfer hydrogenation of polycarbonate.

With respect to green and sustainable chemistry this catalytic protocol contributes in several ways. It represents an example of the utilization of CO_2 as a C1 building block which may lead to the production of commodities and fuels (MeOH) from CO_2. Compared to other transfer hydrogenation systems for cyclic carbonates the present protocol uses a catalyst based on iron which is an earth-abundant metal. In this protocol, isopropanol or ethanol (which can be obtained from renewable resources) is employed as hydrogen sources for the reduction, thus avoiding the handling of flammable hydrogen under high pressure. Notably, the oxidized products, namely acetone and acetaldehyde, respectively, are also valuable products. Thus, overall no waste is produced in this reaction. The chemical recycling of plastics become more and more important. In this respect it is of interest that the reported catalytic system is also capable of depolymerising commercially available poly(propylene carbonate) to propylene glycol and methanol.

Conclusions

In conclusion, we have demonstrated the use of an earth-abundant metal-based catalyst for the transfer hydrogenation of cyclic carbonates using a PNP pincer-type iron complex. Various cyclic carbonates were converted into the respective diols and MeOH. Notably, the reduction of ethylene carbonate which is an intermediate in Shell's OMEGA process led to MeOH in 90% yield. Moreover, this catalytic system proved to be suitable for the depolymersation of poly(propylene carbonate) by transfer hydrogenation which is currently under further investigations in our group.

Experimental

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The complexes **1–6** were prepared using standard Schlenk techniques or a glove box. Complexes **1**, **2**, **3**, **4**, **5** and **6** were prepared according to literature procedures. The analytical data of the iron complexes are consistent with those previously reported in the literature.[45-48] Carbonate **7b** was obtained from abcr GmbH and used without further purification. Carbonate **7k** was obtained from Sigma-Aldrich and used without further purification. Carbonates **7a**, **7c**, **7d**, **7e**, **7f**, **7g**, **7h**, **7i** and **7j** were prepared according to our previously reported protocol. The analytical data were consistent with those previously reported in the literature. [49]

General procedure for the preparation of carbonates (GP1)

A 45 cm3 autoclave was charged with 5 mol% CaI_2, 5 mol% poly(ethylene glycol) dimethyl ether (PEG DME, Mn ~500 g·mol-1) and the respective epoxide. The reactor was sealed and charged with 1–10 bar CO_2. The reaction mixture was stirred for 3–34 h at 25–45 °C. Subsequently the reactor was cooled <20°C with an ice bath and the CO_2 was released slowly. The reaction mixture was filtered over silica gel (SiO_2) with cyclohexane/ethyl acetate. After removal of all volatiles in *vaccuo* the respective carbonate **7** was obtained.

General procedure for the transfer hydrogenation of cyclic carbonates 7a–7k using catalyst 3 (GP2)

In a Schlenk vessel, complex **3** (24 mg, 0.050 mmol) and KO*t*Bu (5.6 mg, 0.050 mmol) were dissolved in THF (1.0 mL) under argon. The mixture was stirred for 5 min at 23 °C. Subsequently, the cyclic carbonate **7** (1.0 mmol) and *i*PrOH (4.0 mL) were added in one portion. The Schlenk vessel was placed in a preheated oil bath (140 °C) and the mixture was stirred for 6–24 h. The reaction mixture was cooled to 23°C and subsequently cooled to 0°C in an ice bath for 1 h. The residual H_2 was released carefully and the mixture was analyzed by GC with mesitylene as the internal standard to determine the MeOH yield. After removal of all volatiles in *vacuo* the crude mixture was purified by column chromatography on silica gel (SiO_2) with cyclohexane/ EtOAc as eluent. After removal of all volatiles *in vacuo* the respective diols (**8a–8j**) were obtained.

General procedure for the transfer hydrogenation of poly(propylene carbonate) (PPC) (GP3)

In a Schlenk vessel, Complex **3** (24 mg, 0.050 mmol) and KO*t*Bu (5.6 mg, 0.050 mmol) were dissolved in THF (1.0 mL) under argon. The mixture was stirred for 5 min at 23 °C. Subsequently poly(propylene carbonate) (average M_n of ~$50{\cdot}10^3$ g·mol^{-1} by GPC, 1.0 mmol) and *i*PrOH (4.0 mL) were added in one portion. The mixture was placed in a preheated oil bath (140 °C) and stirred for 30 h. The reaction mixture was cooled to 23°C and subsequently cooled to 0°C in an ice bath for 1 h. The residual H_2 was released carefully and the mixture was analyzed by GC with mesitylene as the internal standard to determine the MeOH and diol **8c** yield.

4-Ethyl-1, 3-dioxolan-2-one (7a)[49]

Following **GP-1**, 1,2-epoxybutane (41.6 g, 28.0 mmol), CaI_2 (1.70 mg, 5.78 mmol), PEG DME (2.88 mg, 5.76 mmol) and CO_2 (10 bar) were reacted at 25 °C for 24 h. The product **7a** (65.5 g, 564 mmol, 98%) was obtained as a colourless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ= 4.75–4.55 (m, 1H), 4.47 (dd, *J*= 8.4, 7.9 Hz, 1H), 4.03 (dd, *J*= 8.4, 7.0 Hz, 1H), 1.86–1.57 (m, 2H), 0.96 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 155.17, 78.06, 69.05, 26.91, 8.47 ppm.

4-Methyl-1, 3-dioxolan-2-one (7c)[49]

Following **GP-1**, 1,2-epoxypropane (1.96 g, 33.7 mmol), CaI_2 (5.06 mg, 1.72 mmol), PEG DME (861 mg, 1.72 mmol) and CO_2 (10 bar) were reacted at 25 °C for 24 h. The product **7c** (3.24 g, 31.7 mmol, 94%) was obtained as a colourless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ= 4.93–4.73 (m, 1H), 4.53 (ddt, *J*= 8.4, 7.7, 0.7 Hz, 1H), 3.99 (ddt, *J*= 8.3, 7.2, 0.7 Hz, 1H), 1.52–1.32 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 155.14, 73.69, 70.71, 19.32 ppm.

4-Butyl-1, 3-dioxolan-2-one (7d)[49]

Following **GP-1**, 1,2-epoxyhexane (2.04 g, 20.1 mmol), CaI_2 (300 mg, 1.02 mmol), PEG DME (510 mg, 1.02 mmol) and CO_2 (10 bar) were reacted at 25 °C for 24 h. The product **7d** (2.73 g, 19.1 mmol, 94%) was obtained as a colourless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ= 4.79–4.64 (m, 1H), 4.53 (dd, *J*= 8.4, 7.8 Hz, 1H), 4.07 (dd, *J*= 8.4, 7.2 Hz, 1H), 1.87–1.74 (m, 1H), 1.74–1.61 (m, 1H), 1.50–1.30 (m, 4H), 0.97–0.89 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 155.15, 77.12, 69.43, 33.53, 26.42, 22.24, 13.79 ppm.

4-Hexyl-1, 3-dioxolan-2-one (7e)[49]

Following **GP-1**, 1,2-epoxyoctane (2.04 g, 15.9 mmol), CaI_2 (230 mg, 0.783 mmol), PEG DME (390 mg, 0.780 mmol) and CO_2 (10 bar) were reacted at 25 °C for 24 h. The product **7e** (2.71 g, 15.7 mmol, 98%) was obtained as a colourless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ= 4.71 (qd, *J*= 7.5, 5.4 Hz, 1H), 4.60–4.46 (m, 1H), 4.08 (dd, *J*= 8.4, 7.2 Hz, 1H), 1.81 (dddd, *J*= 14.4, 9.4, 5.9, 3.7 Hz, 1H), 1.69 (ddt, *J*= 14.0, 10.7, 5.1 Hz, 1H), 1.55–1.43 (m, 1H), 1.41–1.27 (m, 7H), 0.93–0.86 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 155.12, 77.09, 69.42, 33.88, 31.51, 28.80, 24.33, 22.46, 14.00 ppm.

4-Phenyl-1, 3-dioxolan-2-one (7f)[49]

Following **GP-1**, styrene oxide (1.98 g, 16.5 mmol), CaI_2 (245 mg, 0.834 mmol), PEG DME (414 mg, 0.838 mmol) and CO_2 (10 bar) were reacted at 25 °C for 24 h. The product **7f** (2.51 g, 15.3 mmol, 93%) was obtained as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.57–7.33 (m, 5H), 5.76–5.64 (m, 1H), 4.83 (dd, *J*= 8.6, 8.2 Hz, 1H), 4.37 (dd, *J*= 8.6, 7.9 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 154.79, 135.78, 129.76, 129.26, 125.86, 77.99, 71.17 ppm.

4-Vinyl-1,3-dioxolan-2-one (7g)[49]

Following **GP-1**, butadiene monoxide (2.00 g, 28.5 mmol), CaI_2 (420 mg, 1.42 mmol), PEG DME (714 mg, 1.42 mmol) and CO_2 (10 bar) were reacted at 25 °C for 24 h. The product **7g** (3.08 g, 27.0 mmol, 95%) was obtained as a colourless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ= 6.12–5.77 (m, 1H), 5.51 (dq, *J*= 17.1, 0.9 Hz, 1H), 5.44 (dt, *J*= 10.4, 0.9 Hz, 1H), 5.23–5.05 (m, 1H), 4.61 (dd, *J*= 8.6, 8.1 Hz, 1H), 4.16 (ddd, *J*= 8.2, 7.4, 0.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 154.80, 132.17, 121.25, 77.37, 69.10 ppm.

4-(3-Butenyl)-1,3-dioxolan-2-one (7h)[49]

Following **GP-1**, 1,2-epoxy-5-hexene (1.98 g, 20.2 mmol), CaI_2 (300 mg, 1.02 mmol), PEG DME (510 mg, 1.02 mmol) and CO_2 (10 bar) were reacted at 25 °C for 24 h. The product **7h** (2.70 g, 19.0 mmol, 94%) was obtained as a colourless liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ= 5.80 (ddt, *J*= 17.0, 10.2, 6.7 Hz, 1H), 5.20–5.00 (m, 2H), 4.82–4.68 (m, 1H), 4.55 (dd, *J*= 8.5, 7.9 Hz, 1H), 4.10 (dd, *J*= 8.5, 7.2 Hz, 1H), 2.40–2.10 (m, 2H), 2.07–1.87 (m, 1H), 1.79 (dddd, *J*= 14.0, 8.7, 7.0, 5.2 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 154.96, 136.07, 116.45, 76.33, 69.33, 33.07, 28.67 ppm.

4, 5-Dimethyl-1, 3-dioxolan-2-one (7i)[49]

Following **GP-1**, trans-2,3-dimethyloxirane (2.05 g, 28.4 mmol), CaI_2 (408 mg, 1.3 mmol), PEG DME (694 mg, 1.39 mmol) and CO_2 (20 bar) were reacted at 70 °C for 24 h. The product **7i** (2.78 g, 23.9 mmol, 84%, cis/trans = 1.38/1) was obtained as a colourless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.87-4.77 (m, 2H, cis), 4.36–4.27 (m, 2H, trans), 1.44–1.38 (m, 6H, trans), 1.35–1.29 (m, 6H, cis) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 14.31 (CH_3, cis), 18.29 (CH_3, trans), 76.09 (CH, cis), 79.95 (CH, trans), 154.56 (C=O, trans), 154.67 (C=O, cis) ppm.

4, 4-Dimethyl-1, 3-dioxolan-2-one (7j)[49]

Following **GP-1**, 2,2-dimethyloxirane (2.03 g, 28.2 mmol), CaI_2 (408 mg, 1.3 mmol), PEG DME (694 mg, 1.39 mmol) and CO_2 (10 bar) were reacted at 25 °C for 24 h. The product **7j** (3.02 g, 26.0 mmol, 92%) was obtained as a colourless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.17 (s, 2H, CH_2), 1.55 (s, 6H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 154.60, 81.72, 75.39, 53.49, 26.04 ppm.

1, 2-Butanediol (8a) (Table 2, entry 2)[33]

Following **GP-2**, complex **3** (24 mg, 0.50 mmol), KO*t*Bu (56mg, 0.50 mmol), THF (5.0 mL), 4-ethyl-1, 3-dioxolan-2-one (**7a**, 1.16 g, 10.0 mmol) and *i*PrOH (25 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc = 1:2) the title compound **8a** (646 mg, 7.17 mmol, 72%) was obtained as a colorless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.08 (br s, 2H), 3.64–3.52 (m, 2H), 3.48–3.34 (m, 1H), 1.47 (m, 2H), 0.97 (t, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 73.73, 66.31, 25.95, 9.98 ppm.

1, 2-Propanediol (8c) (Table 2, entry 5)[33]

Following **GP-2**, complex **3** (23.5 mg, 0.05 mmol), KO*t*Bu (5.6 mg, 0.05 mmol), THF (1.0 mL), 4-Methyl-1, 3-dioxolan-2-one (**7c**, 102 mg, 1.0 mmol) and *i*PrOH (4 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc = 1:2) the title compound **8c** (68.7mg, 0.904 mmol, 91%) was obtained as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.38 (br s, 2H), 3.88–3.79 (m, 1H), 3.56–3.51 (m, 1H), 3.36–3.30 (m, 1H), 1.08 (t, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 68.35, 67.97, 18.73 ppm.

1, 2-Hexanediol (8d) (Table 2, entry 6)[33]

Following **GP-2**, complex 3 (23.5 mg, 0.05 mmol), KO*t*Bu (5.6 mg, 0.05 mmol), THF (1.0 mL), 4-butyl-1, 3-dioxolan-2-one (**7d**, 144 mg, 1.0 mmol) and ***i***PrOH (4 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc = 1:2) the title compound **8d** (95.2 mg, 0.807 mmol, 81%) was obtained as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.78–3.27 (m, 5H), 1.47–1.24 (m, 6H), 0.94–0.83 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 77.37, 66.76, 32.78, 27.75, 22.71, 14.00 ppm

1, 2-Octanediol (8e) (Table 2, entry 7)[29]

Following **GP-2**, complex **3** (23.5 mg, 0.05 mmol), KO*t*Bu (5.6 mg, 0.050 mmol), THF (1.0 mL), 4-hexyl-1, 3-dioxolan-2-one (**7e**, 172 mg, 1.0 mmol) and *i*PrOH (4 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc= 1:2) the title compound **8e** (122.3 mg, 0.838 mmol, 84%) was obtained as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.73 (m, 1H), 3.68 (dd, 1H), 3.46 (dd, 1H), 2.52 (br s, 2H), 1.26–1.48 (m, 10H), 0.87 (t, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 72.37, 66.82, 33.16, 31.76, 29.32, 25.53, 22.60, 14.08 ppm.

1-Phenyl-1, 2-ethanediol (8f) (Table 2, entry 8)[33]

Following **GP-2**, complex **3** (23.5 mg, 0.05 mmol), KO*t*Bu (5.6 mg, 0.050 mmol), THF (1.0 mL), 4-Phenyl-1, 3-dioxolan-2-one (**7f**, 164 mg, 1.0 mmol) and *i*PrOH (4 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc = 1:1) the title compound **8f** (114 mg, 0.827 mmol, 83%) was obtained as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.38-7.26 (m, 4H), 4.86–4.80 (m, 1H), 3.81–3.73 (m, 1H), 3.70–3.63 (m, 1H), 3.70–3.63 (m, 1H), 2.74–2.58 (m, 1H), 2.30–2.12 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 140.82, 128.56, 128.03, 126.07, 74.70, 68.09 ppm.

But-3-ene-1,2-diol (8g) (Table 2, entry 9)[50]

Following **GP-2**, complex **3** (23.5 mg, 0.05 mmol), KO*t*Bu (5.6 mg, 0.050 mmol), THF (1.0 mL), 4-vinyl-1,3-dioxolan-2-one (**7g**, 114 mg, 1.0 mmol) and *i*PrOH (4 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc = 1:2) the title compound **8g** (74.2 mg, 0.843 mmol, 85%) was obtained as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.78 (ddd, *J*= 17.3, 10.6, 5.6 Hz, 1H), 5.29 (dt, *J*= 17.3, 1.5 Hz, 1H), 5.15 (dt, *J*= 10.6, 1.4 Hz, 1H), 4.29–4.07 (m, 1H), 3.61 (dd, *J*= 11.4, 3.3 Hz, 1H), 3.43 (dd, *J*= 11.3, 7.5 Hz, 1H), 2.93 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 136.69, 116.75, 73.31, 66.23 ppm.

5-Hexene-1,2-diol (8h) (Table 2, entry 10)[51]

Following **GP-2**, complex 3 (23.5 mg, 0.05 mmol), KO*t*Bu (5.6 mg, 0.050 mmol), THF (1.0 mL), 4-(3-butenyl)-1,3-dioxolan-2-one (**7h**, 142 mg, 1.0 mmol) and *i*PrOH (4 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc = 1:2) the title compound **8h** (82.0 mg, 0.707 mmol, 71%) was obtained as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.75 (ddt, *J*= 16.8, 10.2, 6.6 Hz, 1H), 5.06–4.84 (m, 2H), 4.11–3.10 (m, 5H), 2.31–1.88 (m, 2H), 1.43 (t, *J*= 6.5 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 138.08, 115.00, 71.73, 66.62, 32.14, 29.97 ppm.

2, 3-Butanediol (8i) (Table 2, entry 11)[25]

Following **GP-2**, complex **3** (23.5 mg, 0.05 mmol), KO*t*Bu (5.6 mg, 0.050 mmol), THF (1.0 mL), 4, 5-dimethyl-1, 3-dioxolan-2-one (**7i**, 142 mg, 1.0 mmol) and *i*PrOH (4 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc= 1:3) the title compound **8i** (77.1 mg, 0.857 mmol, 86%) was obtained as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.80–3.74 (m, 2H, *cis* isomer), 3.53–3.48 (m, 2H, *trans* isomer), 2.57–2.02 (m, 2H), 1.17–1.11 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 72.2, 70.7, 19.0 16.7 ppm.

2-Methyl-1, 2-propanediol (8j) (Table 2, entry 12)[25]

Following **GP-2**, complex **3** (23.5 mg, 0.05 mmol), KO*t*Bu (5.6 mg, 0.050 mmol), THF (1.0 mL), 4, 4-dimethyl-1, 3-dioxolan-2-one (**7j**, 142 mg, 1.0 mmol) and *i*PrOH (4 mL) were reacted. After column chromatography (SiO_2, cyclohexane/EtOAc = 1:2) the title compound **8j** (82.4 mg, 0.915 mmol, 92%) was obtained as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.18 (br s, 2H), 1.52 (s, 6H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ= 154.60, 81.72, 75.39, 53.49, 26.04 ppm.

Conflicts of interest

There are no conflicts of interest to declare.

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