DOI: 10.1002/adsc.201201070

Stereochemical Divergence in the Formation of Organic Carbonates Derived from Internal Epoxides

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Received: December 6, 2012; Revised: January 16, 2013; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201201070.

Abstract: Catalysis of the challenging cycloaddition of carbon dioxide to internal epoxides has been studied using iron(III) amine triphenolate complexes and particular focus has been given to the stereochemical regulation of this process. When pure *cis*- or *trans*-2,3-epoxybutane is used as substrate, the stereochemistry of the product can be controlled yielding selectively *cis*- or *trans*-cyclic carbonates for both epoxidic substrates. This stereochemical divergence relates to two accessible catalytic pathways leading to either the *cis* or *trans* product *via* two distinct ring-closure steps. The involved mechanism and stereocontrol is a function of the catalyst/co-catalyst loading, and is further influenced by the medium, temperature and catalyst/co-catalyst structure. Other *trans*-internal epoxides could also be successfully converted into the pure *trans*-cyclic carbonate products without any loss of stereochemical information.

Keywords: carbon dioxide fixation; cycloaddition; homogeneous catalysis; iron; stereoselectivity

Introduction

The field of carbon dioxide catalysis is currently a thriving area of research providing improved and new carbon fixation methodologies.[1–3] These methods allow for the conversion of a waste material into various value-added organics and CO_2 can be considered as an alternative and renewable carbon feedstock for a number of fossil fuel-based chemicals.[4,5] One successful example of CO_2 utilization is the atom-efficient synthesis of cyclic organic carbonates through addition of CO_2 to terminal epoxides which has been extensively investigated,[6–8] whilst the use of the more challenging internal epoxides as substrates has historically received much less attention. Cyclic carbonates offer potential building blocks during the synthesis of pharmaceutical and fine chemical intermediates, amongst other useful applications.[9]

The most popular and successful type of catalyst system for the cycloaddition of CO_2 to epoxides consists of a Lewis acid site or metal complex and a nucleophilic co-catalyst (i.e., a binary system),[10–17] and the latter may also be incorporated into the catalyst structure resulting in a bifunctional mediator.[18–20] Whereas the easy conversion of terminal epoxides into their cyclic carbonates can be mediated by many catalyst systems, there remain important synthetic challenges to be solved. Amongst these challenges are the efficient conversion of internal epoxides,[11,16,21–25] the asymmetric synthesis of carbonates[10,26–30] and the preparation of enantioenriched polycarbonates.[31–35] Stereocontrol in organic carbonate synthesis is a topic that has recently become an important objective as the properties of both cyclic as well as polycarbonates depend on the relative configuration of pending substituents and the degree of stereoregularity.

For instance, *cis*-2,3-epoxybutane is a liquid whereas *trans*-2,3-epoxybutane is a solid under ambient conditions. Furthermore, Darensbourg and co-workers have recently shown that polycarbonates derived from (chiral) epichlorohydrin[36] and styrene oxide[37] may suffer from some loss of stereochemical information (up to 20%) due to ring-opening at both the methine as well as methylene carbon centres (Figure 1) of the epoxidic substrate, resulting in formal inversion and retention of configuration, respectively. This stereodivergence in polycarbonate formation remains a crucial aspect to control as it affects important polymer properties such as the glass transition temperature, stereoregularity and thermal stability.

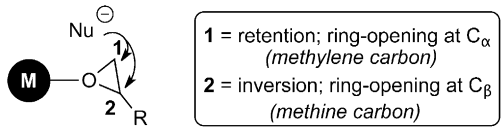


Figure 1. Ring-opening mediated by a nucleophile at both the methylene carbon (C_α) and methine carbon (C_β) potentially leading to loss of stereo-information. M here denotes a metal catalyst.

As stated, most of the catalyst systems described to date for the cycloaddition of CO_2 to epoxides display ample scope for the conversion of terminal epoxides as internal epoxides are significantly more difficult to convert. The simplest internal epoxide is 2,3-epoxybutane, for which there are limited examples of Co-, Fe-, Cr-, Sn- and V-based catalyst systems capable of converting it into the cyclic carbonate product, albeit with different degrees of efficiencies.[11,16,21–25] Interestingly, examples of the conversion of this substrate typically start from either pure *cis*- or *trans*-2,3-epoxybutane and in most cases the reported cyclic carbonate products show some loss of stereochemistry from the original configuration of the starting epoxide. This slight loss of configuration cannot be explained by the generally involved combination of two S_N2 reactions taking place at the ring-opening and ring-closure stage of the process, as this would lead to an overall retention of configuration.

Inspired by these latter results and their relationship with the challenging and important stereoregular formation of polycarbonates, we here communicate the conversion of internal epoxides with a series of iron(III) amine triphenolate catalysts into their respective carbonates. This work has focused particularly on the stereochemical manipulation in these reactions in order to gain a deeper understanding on how to increase the stereoregulation.

Results and Discussion

The iron(III) amine triphenolate complexes **1** and **2** used in this study (Figure 2) have been previously reported[21,22] and complex **3** was synthesized in a similar manner from the corresponding amine triphenol ligand.

Initially, the stereochemistry obtained from the conversion of 2,3-epoxybutane was investigated as previous work showed that under certain conditions some loss of configuration from the starting epoxide was noted.[21] In order to investigate this observation in more detail, the effect of the tetrabutylammonium bromide (TBAB)[38] loading on the ratio of *cis*- and *trans*-cyclic carbonate products from the conversion of *cis*-2,3-epoxybutane was studied, using complexes **1** and **3** as catalysts (see Table 1). Interestingly, the

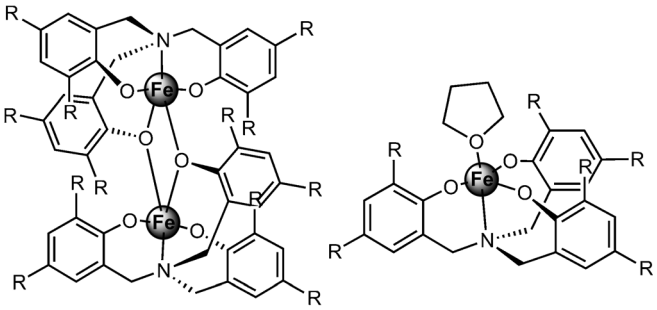
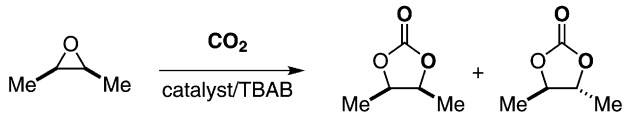


Figure 2. Iron(III) amino triphenolate complexes **1–3** used in this study.

relative configuration of the methyl groups in the cyclic carbonate product appears to have a strong dependence on the TBAB loading. In addition, and as would be expected, it can be seen that upon reducing the TBAB loading, also the isolated yield decreases.

Complex **1** is able to selectively catalyze the conversion of *cis*-2,3-epoxybutane to the corresponding *cis*-cyclic carbonate (i.e., retention of configuration) at higher TBAB loadings (Table 1, entry 1), at a low TBAB loading of 0.125 mol% (0.25 equiv. of TBAB per Fe centre) this catalyst system is able to form the

Table 1. Conversion of *cis*-2,3-epoxybutane into *cis*- and *trans*-cyclic carbonate products using complexes **1** and **3**.[a]



Entry	Catalyst	TBAB [mol%]	*cis*[b] [%]	*trans*[b] [%]	Yield[c] [%]
1	**1**	4.0	>99	<1	68
2	**1**	2.5	95	5	47
3	**1**	1.25	69	21	32
4	**1**	0.625	26	74	30
5	**1**	0.313	18	82	26
6	**1**	0.125	11	89	19
7	**3**	4.0	94	6	72
8	**3**	2.5	84	16	61
9	**3**	1.25	22	78	56
10	**3**	0.625	18	82	52
11	**3**	0.313	5	95	48
12	**3**	0.125	<1	>99	41

[a] *Conditions:* *cis*-2,3-epoxybutane (1.0 g), catalyst = **1** (0.25 mol%), or **3** (0.5 mol%), TBAB (loading indicated), 80 °C, 18 h, 10 bar initial CO_2 pressure in a 30 mL autoclave.

[b] Determined by ^{1}H NMR ($CDCl_3$) from the isolated product.

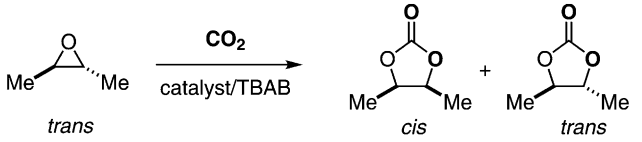
[c] Isolated yield, and selectivity for the cyclic carbonate products in all cases was >99%.

trans-cyclic carbonate (Table 1, entry 6) with 89% selectivity.

Complex **3** is able to exclusively form the *trans*-cyclic carbonate from *cis*-2,3-epoxybutane at a TBAB loading of 0.125 mol% (Table 1, entry 12). The occurrence of two different products and the strong effect of the TBAB loading indicate that there are likely to be two different ring-closure mechanisms operating during the cycloaddition reaction, one resulting in formal retention of configuration and the other one leading to formal inversion of configuration.

In order to further investigate the effect of TBAB loading on the configuration of the cyclic carbonate products and gain further insight into the proposal of two ring-closure mechanisms, *trans*-2,3-epoxybutane was also studied as substrate for this reaction (Table 2).[39] It can be seen that both complexes **1** and **3** selectively convert *trans*-2,3-epoxybutane into the *trans*-cyclic carbonate products at TBAB loadings of 2.5 and 1.25 mol%, respectively (Table 2, entries 1 and 7). In addition, when complex **2** was used as catalyst, even at a low catalyst loading of 0.313 mol%, selectivity towards the *trans*-cyclic carbonate is observed (Table 2, entry 6), which is different to the behaviour observed using complexes **1** and **3** at this TBAB loading; in these latter cases significant amounts of the *cis*-cyclic carbonate are obtained (Table 2, entries 4 and 9, 45% and 36%). At a very low TBAB loading of 0.0625 mol% and a 0.5 mol% loading of complex **1** (0.0625 equiv. of TBAB per Fe centre) using an extended reaction time of 66 h, 55% of the *cis*-cyclic carbonate could be obtained (Table 2, entry 5). The conversion of *trans*-2,3-epoxybutane into the *cis*-cyclic carbonate product is extremely challenging as a result of the *trans*-cyclic carbonate being the thermodynamically favoured product. If the temperature of the reaction is decreased from 80 to 50 °C, a successive increase in the *cis*-cyclic carbonate product is observed, with up to a remarkable 85% formation of the *cis*-cyclic carbonate, although at the expense of the overall yield (Table 2, entries 10–12).

Table 2. Conversion of *trans*-2,3-epoxybutane into *cis*- and *trans*-cyclic carbonate products using complexes **1**–**3**.[a]

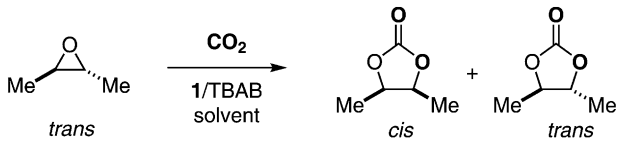


Entry	Catalyst	TBAB [mol%]	*cis*[b] [%]	*trans*[b] [%]	Yield[c] [%]
1	**1**	2.5	<1	>99	67
2	**1**	1.25	6	94	58
3	**1**	0.625	30	70	36
4	**1**	0.313	45	55	23
5[d]	**1**	0.0625	55	45	28
6	**2**	0.313	<1	>99	23
7	**3**	1.25	<1	>99	71
8	**3**	0.625	9	91	59
9	**3**	0.313	36	64	32
10[e]	**1**	0.0625	66	34	20
11[f]	**1**	0.0625	76	24	12
12[g]	**1**	0.0625	85	15	6

[a] *Conditions: trans*-2,3-epoxybutane (1.0 g), catalyst; **1** or **2** = 0.25 mol%, **3** = 0.5 mol%, TBAB (loading indicated), 80 °C, 18 h, 10 bar initial CO_2 pressure in a 30 mL autoclave.
[b] Determined by ^{1}H NMR ($CDCl_3$) from the isolated product.
[c] Isolated yield, and selectivity for the cyclic carbonate products in all cases was >99%.
[d] 0.5 mol% of **1**, 66 h.
[e] 0.5 mol% of **1**, 70 °C, 66 h.
[f] 0.5 mol% of **1**, 60 °C, 66 h.
[g] 0.5 mol% of **1**, 50 °C, 90 h.

The initial screening experiments were performed without the presence of solvent, therefore the substrate and cyclic carbonate products play this role and therefore in order to investigate the effects of changing the medium in which the reaction occurs, different solvents were tested (Table 3). Under the conditions used, all reactions carried out using a co-solvent resulted in lower overall yields due to the dilution of the reaction mixture and hence lower conversion levels. The use of methyl ethyl ketone (MEK) or acetonitrile (MeCN) results in a reduced amount of *cis*-cyclic carbonate product (Table 3, entries 2 and 3) compared to the reaction without co-solvent. This is likely a result of the coordinating potential of these solvents and their polarity leading to bulk stabiliza-

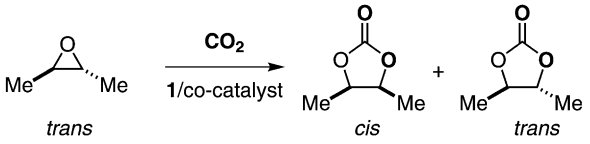
Table 3. Variation of solvent during the conversion of *trans*-2,3-epoxybutane into *trans*- and *cis*-cyclic carbonate products using complex **1**.[a]



Entry	Solvent	*cis*[b] [%]	*trans*[b] [%]	Yield[c] [%]
1	none	54	46	32
2	MEK	22	78	18
3	MeCN	30	70	12
4	$CHCl_3$	44	56	18
5	toluene	50	50	15

[a] *Conditions: trans*-2,3-epoxybutane (0.50 g), catalyst = **1** (0.5 mol%), TBAB (0.0625 mol%), solvent (1.0 mL), 80 °C, 66 h, 10 bar initial CO_2 pressure in a 30 mL autoclave.
[b] Determined by ^{1}H NMR ($CDCl_3$) from the isolated product.
[c] Isolated yield, and selectivity for the cyclic carbonate products in all cases was >99%.

Table 4. Variation of co-catalyst structure during the conversion of *trans*-2,3-epoxybutane into *trans*- and *cis*-cyclic carbonate products using complex **1**.[a]



Entry	Co-catalyst	*cis*[b] [%]	*trans*[b] [%]	Yield[c] [%]
1	TBAC	46	54	47
2	TBAB	48	52	77
3	TBAI	33	67	64
4	PPN-Br	28	72	63
5	PPN-Cl	26	74	46

[a] *Conditions:* *trans*-2,3-epoxybutane (0.50 g), catalyst = **1** (0.5 mol%), co-catalyst (0.313 mol%), 80 °C, 66 h, 10 bar initial CO_2 pressure in a 30 mL autoclave. TBAC = tetrabutylammonium chloride; TBAI = tetrabutylammonium iodide; PPN = bis(triphenylphosphoranylidene)ammonium.

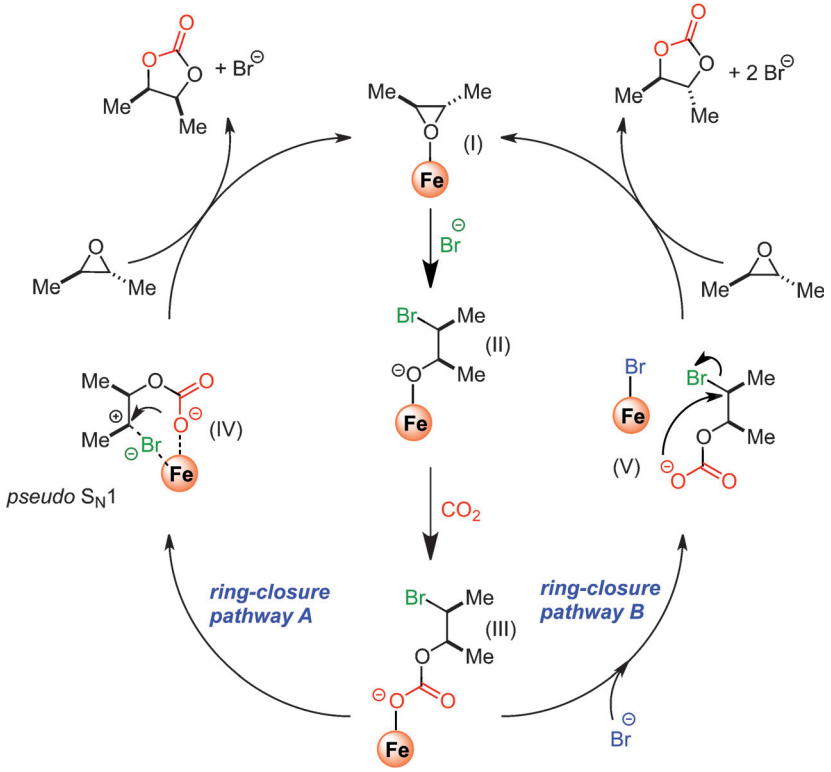
[b] Determined by ^{1}H NMR ($CDCl_3$) from the isolated product.

[c] Isolated yield, and selectivity for the cyclic carbonate products in all cases was >99%.

tion of intermediates in the ring-closure event leading to formal retention of configuration. In contrast, the use of chloroform ($CHCl_3$) and toluene result in little difference in the amount of *cis*-cyclic carbonate obtained (Table 3, entries 4 and 5) compared with the case where no co-solvent is used.

The effect of halide nucleophile and variation of the counter ion has also been studied (Table 4). The results reveal that the tetrabutylammonium based co-catalysts result in higher yields and selectivities for the *cis*-cyclic carbonate products compared with the bis(triphenylphosphoranylidene)ammonium-based co-catalysts. These results also indicate that the highest yield and selectivity is obtained when using TBAB.

The combined results obtained in this study allow us to propose that there exist two distinct ring-closure mechanisms during the cyclic carbonate product formation. Both of these proposed mechanisms are shown in Scheme 1 and are in line with the catalytic findings reported in Table 1, Table 2, Table 3 and Table 4. The first step in the mechanism is coordination of the epoxide substrate (in this case *trans*-2,3-epoxybutane, intermediate I), then subsequent ring-opening of the epoxide by the bromide anion (intermediate II), which results in an inversion of configuration at this carbon atom. After insertion of CO_2 there are two possible ring-closure steps. In pathway A (i.e., at a relatively low concentration of TBAB), the ring-closure is controlled by the metal catalyst



Scheme 1. Proposed ring-closure mechanisms (substrate = *trans*-2,3-epoxybutane) occurring in the coordination sphere of the Fe complex (pathway A) resulting in formal inversion of configuration, and outer-sphere ring-closure (pathway B) resulting in formal retention of configuration.

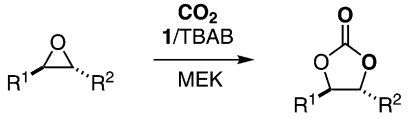
with the linear carbonate anion coordinated. Amino triphenolate Fe complexes with small *ortho* substituents (cf., **1** and **2**) have been shown to be able to form hexacoordinated complexes[22] with an available *cis*-coordination potential unlike in the case of, for instance, metallosalens.[8] The bromide in intermediate III is proposed to dissociate from the coordinated linear carbonate towards the metal complex using the vacant *cis*-coordination site on the metal centre; then, the resultant sp^2-hybridized carbon centre undergoes a *pseudo*-S_N1 type ring-closure and hence an overall inversion of the configuration occurs.

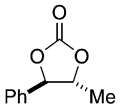
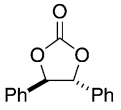
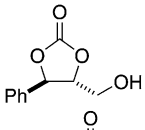
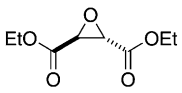
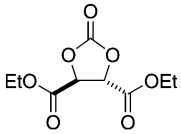
The other pathway B (Scheme 1) is associated with a relatively high concentration of bromide anions in the reaction mixture. As a consequence, there is competition between coordination of the linear carbonate anion and the excess bromide anions resulting in a higher probability for an outer-sphere ring-closure step. This seems to be supported by the observation that polar solvents favour the formation of the *trans*-carbonate product (Table 3) as these solvents are more effective in stabilizing the anion in intermediate V. Thus, in this case the ring-closure follows a typical S_N2 type elimination of the bromide and hence a second inversion occurs at this carbon atom, resulting in an overall retention of configuration (i.e., formation of the *trans* product). The absence of any polymeric products in the ^{1}H NMR spectra of the crude products leads us to believe that the formation of the inversion product is not *via* a depolymerisation route as suggested by Kruper and co-workers for their Cr(III) porphyrinate catalyst system.[23]

In order to further exemplify the potential for retention of configuration in the epoxide substrate, we have converted four other internal *trans*-epoxides into the corresponding *trans*-cyclic carbonates with >99% retention of configuration in high isolated yields (Table 5). The ability of this complex to convert these epoxides into the cyclic carbonate products also exemplifies the power of this catalyst system as there are very few examples of catalyst systems able to convert this type of challenging substrates. We chose to use MEK as solvent due to the solid nature of the products, allowing optimal yields to be obtained. The *trans* nature of the products was also confirmed by the absence of cross-peaks in the ^{1}H NOESY NMR spectra.

Preliminary investigations with cyclohexene oxide (a cyclic oxirane) as substrate using Fe catalyst **1** and a high and low TBAB loading indicate that also in these cases stereochemical divergence can be observed for the cyclic carbonate product with the *cis*-product (with 97% selectivity) almost exclusively formed at a high loading of TBAB (2.5 mol%) while isolating the *trans* carbonate as the most prominent species (with 72% selectivity) at a low TBAB loading (0.157 mol%). However, in this particular case the interpretation of the data[40] is complicated as the cyclic carbonate can also arise from the main product formed under these conditions (polycyclohexene carbonate, see the Supporting Information) by several different types of back-biting mechanisms.[41] These latter results may hold relevance to enantioselective CO_2/cyclohexene oxide couplings to afford chiral carbonate-based polymers.[42]

Table 5. Cycloaddition of carbon dioxide to internal epoxides catalyzed by **1**.[a]



Entry	Substrate	Product	Yield[b,c] [%]
1			>99
2			>99
3			85
4			87

[a] *Conditions:* Substrate (1.52 mmol), catalyst = **1** (2.0 mol%), co-catalyst (5.0 mol%), 80 °C, 66 h, 10 bar initial CO_2 pressure in a 30 mL autoclave.

[b] Determined by ^{1}H NMR ($CDCl_3$) from the isolated product.

[c] Isolated yield, and selectivity for the cyclic carbonate products in all cases was >99% with >99% selectivity for the *trans* isomer.

Conclusions

In summary, we have found an interesting stereochemical control in the formation of cyclic carbonates derived from internal epoxides. The effect of co-catalyst loading and other factors on these conversions was studied in detail and two distinct ring-closure mechanisms are proposed leading to a formal retention or inversion of the relative configuration of both substituents in the starting epoxide. The formal inversion process is proposed to be controlled in the coordination sphere of the metal stemming from a *pseudo* S_N1 process, whereas the observation of retention is due to two consecutive S_N2 processes at the same

carbon centre occurring in the ring-opening and ring-closure steps of the mechanism.

The catalyst system **1** has also been shown to be able to convert other *trans*-internal epoxides whereby selectively *trans*-cyclic carbonates are formed. The knowledge obtained through these studies is highly important in the context of asymmetric synthesis of cyclic carbonate derivatives, and also provides further insight for the preparation of chiral polycarbonates of which the properties depend on the stereoregularity of the polymer backbone.

Experimental Section

General Methods

The synthesis of the iron(III) amine triphenolate complex, **3**, was carried out using standard vacuum line, Schlenk or cannular techniques and once synthesized the compound was stored in a vial kept in air. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. IR spectra were obtained using a Bruker Alpha FT-IR spectrometer. Mass spectrometric analysis and X-ray diffraction studies were performed by the Research Support Group at the ICIQ.

Reagents

All substrates are commercially available and were used as received. Methyl ethyl ketone (MEK), all other reagents and carbon dioxide (purchased from PRAXAIR) were used as received without further purification or drying prior to their use. The ligands used during the synthesis of complexes **1–3** were synthesized as described previously.[21,22,43]

Preparation of Complex 3

A tetrahydrofuran solution (30 mL) of the requisite amino triphenol ligand (1.0 g, 1.49 mmol) was slowly added to a suspension of sodium hydride (107 mg, 4.46 mmol) in tetrahydrofuran (10 mL). The suspension was stirred overnight and then added to anhydrous iron(III) chloride (241 mg, 1.49 mmol), whereby the suspension immediately turned dark brown. The mixture was stirred for a further 5 h before being filtered through a pad of Celite® and the solvent removed under reduced pressure to afford a brown powder; yield: 998 mg (84%). Crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of a tetrahydrofuran solution of the complex and the structure and refinement parameters can be found in the Supporting Information.[44] HR-MS (MALDI^{+}, dctb): $m/z = 724.4487$, calcd. for $[M-THF]^{+}$: 724.4392; IR (neat): $\nu = 2953$ (m), 2902 (w), 2867 (w), 1682 (vw), 1604 (vw), 1466 (m), 1438 (m), 1413 (w), 1389 (vw), 1361 (m), 1302 (w), 1260 (s), 1239 (s), 1204 (w), 1169 (m), 1131 (w), 1067 (w), 1028 (w), 979 (vw), 914 (w), 875 (m), 837 (s), 810 (w), 773 (w), 749 (m), 693 (w), 646 (w), 605 (m), 554 (s), 483 (s), 450 (vw), 432 (vw), 387 cm^{-1} (m); UV-Vis (toluene): λ (ε in $L\,mol^{-1}\,cm^{-1}$) = 424 nm (4570), 332 nm (5460).

Typical Catalytic Experiment

To a 30-mL stainless steel reactor equipped with a stirrer bar and containing 2,3-epoxybutane (1.0 g) was added catalyst **1** (32.5 mg, 0.25 mol%) and TBAB (89 mg, 2.5 mol%). Three cycles of pressurization and depressurization of the reactor (with carbon dioxide at 5 bar) were carried out before finally stabilizing the pressure at 10 bar. The reactor was then heated at 80 °C with stirring for 18 h. After this time, the reactor was cooled to room temperature and the unreacted epoxide removed under reduced pressure. The residue was passed through a silica pad using dichloromethane as the eluent and the solvent removed under reduced pressure to yield analytically pure cyclic carbonate product.

Product Characterization

All purified cyclic carbonate products obtained were characterized by ^{1}H, $^{13}C\{H\}$ NMR and IR spectrometry. HR-MS analyses were obtained for all compounds that have not been previously reported. All original spectra and tabular data can be found in the Supporting Information.

Acknowledgements

We thank ICIQ, ICREA, the Spanish Ministerio de Economía y Competitividad (MINECO) through project CTQ2011-27385. We thank Giovanni Salassa for help with the DFT calculations.

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