# Aluminum(salen) Complexes as Catalysts for the Kinetic Resolution of Terminal Epoxides via CO_2 Coupling

Michael North,* Sophie C. Z. Quek, Natalie E. Pridmore, Adrian C. Whitwood, and Xiao Wu

Department of Chemistry, University of York, Heslington, York, YO10 5DD, U.K.

S Supporting Information

ABSTRACT: The development of inexpensive and sustainable aluminum(salen) complexes as catalysts for the kinetic resolution of terminal epoxides is described. The kinetic resolution is carried out under mild conditions (0−25 °C and 1 bar of CO_2 pressure) in the presence of tetrabutylammonium bromide as co-catalyst in the absence of solvent. The relative rate of reaction of the two epoxide enantiomers (k_{rel}) is substrate dependent, and the highest k_{rel} obtained was 15.4, using N-(2,3-epoxypropyl)diphenylamine as substrate.

Al(salen)OAc / Bu$_4$NBr (2.5 mol%)
0 °C, 1 atm CO_2

k_{rel} upto 15.4
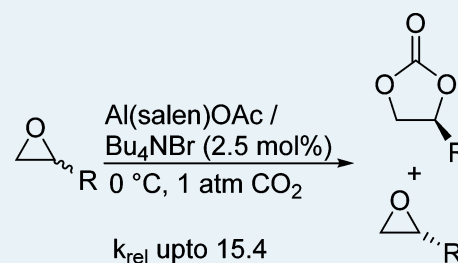
KEYWORDS: kinetic resolution, epoxide, cyclic carbonate, aluminum(salen), catalysis

Cyclic carbonates **1** (Figure 1) such as racemic propylene carbonate **1a** and ethylene carbonate **1b** have a wide range of
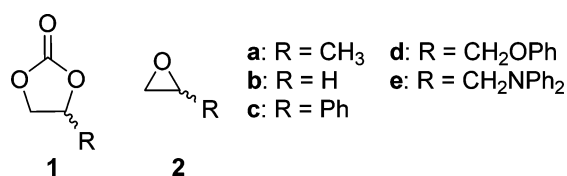

a: R = CH$_3$ d: R = CH$_2$OPh
b: R = H   e: R = CH$_2$NPh$_2$
c: R = Ph

1 **2**

Figure 1. Structures of cyclic carbonates **1** and epoxides **2**.

industrial applications.[1] They may be utilized as extraction media, electrolytes, and solvents for the production of plastics[2] or as superior alternatives to conventional cleaning agents.[3] In addition to these uses as inert materials, they may be converted into various ureas, esters, and amino acids.[4] These intermediates may then be used in the manufacture of pharmaceuticals, where chirality is critical to the activity of the product.

Although cyclic carbonate synthesis may be achieved by many different means,[5] the route using epoxides and carbon dioxide as starting materials (Scheme 1) is of particular importance as a 100% atom-economical reaction that utilizes carbon dioxide as a sustainable chemical feedstock.[6] We have previously shown that the combination of bimetallic aluminum-(salen) complex **3a** and tetrabutylammonium bromide would catalyze the synthesis of cyclic carbonates **1** from terminal epoxides and carbon dioxide at room temperature and atmospheric pressure.[7] Complex **3a** and related immobilized catalysts were shown to be compatible with impure carbon dioxide such as that present in power station flue gas[6b,8] or even in the atmosphere.[9]

Nonracemic epoxides are valuable synthetic intermediates that are often prepared by asymmetric epoxidation[10] or kinetic resolution during ring opening of epoxides by water catalyzed

Scheme 1. Synthesis of Cyclic Carbonates 1

2.5 mol% **3a**, 2.5 mol% Bu$_4$NBr
25 °C, 1 atm CO_2, neat

3a
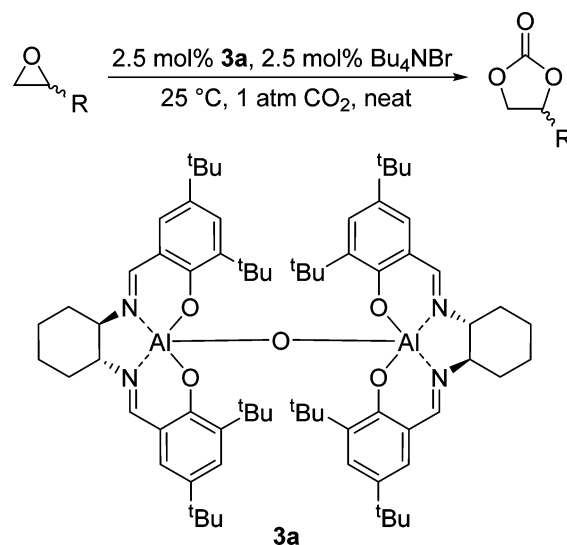
by Co(III)(salen) complexes[11] or by trimethylsilyl azide catalyzed by Cr(III)(salen) complexes.[12] These two epoxide ring-opening reactions have been shown to be extremely general, giving k_{rel} values of at least 45 over a range of substrates. Jacobsen has carried out a detailed experimental and theoretical mechanistic study of the hydrolytic kinetic resolution of epoxides catalyzed by Co(salen) complexes.[13] This study indicated that the reaction was bimolecular in Co(salen) catalyst, and the structure of the key stereo-determining transition state explains the generality of the
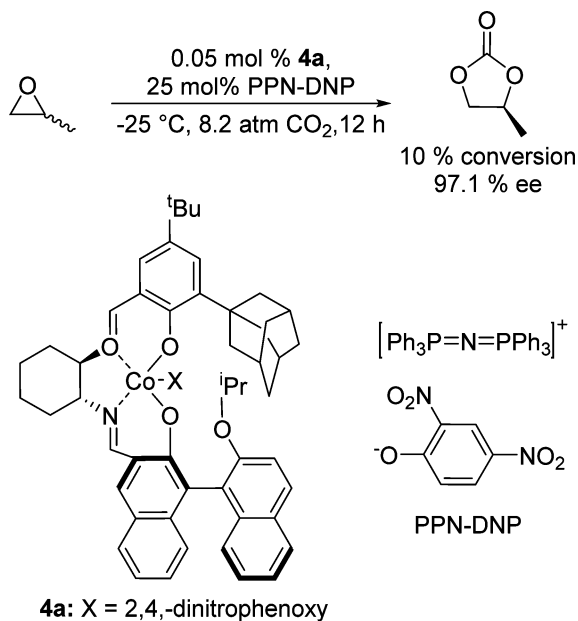
reaction as the epoxide substituent is oriented to an empty region of space while the kinetic resolution is a consequence of the stepped salen ligand.

Complex **3a** is enantiomerically pure, and therefore, the potential exists for it to carry out a kinetic resolution of racemic epoxides leading to enantiomerically enriched epoxides and/or cyclic carbonates. However, no kinetic resolution was observed during the conversion of styrene oxide into styrene carbonate **1c** using complex **3a**. Nevertheless, when (R)-styrene oxide ((R)-**2c**) was used as substrate, cyclic carbonate **1c** was obtained in enantiomerically pure form, indicating preservation of stereochemistry.[7a] A separate study by Ren et al. using single-component aluminum(salen) catalysts also showed retention of epoxide stereochemistry.[14]

There has been limited previous work on kinetic resolution of epoxides by cyclic carbonate synthesis. The earliest reports came from the group of Vogt using titanium or vanadium binol complexes, but these catalysts gave k_{rel} values of only 1.5−2.6.[15] Subsequently, Dibenedetto et al. showed that niobium(IV) phosphine complexes would give styrene carbonate with up to 22% enantiomeric excess,[16] and Jiang obtained k_{rel} values up to 3.2 for the kinetic resolution of propylene oxide **2a** using a chiral Ni(salen) complex incorporated within a MOF.[17] However, by far the most studied and successful catalyst systems developed to date are those based on chiral Co(III)(salen)[18,19] or Co(III)(acen)[20] complexes. The most effective of these is the combination of complex **4a** and PPN−DNP, which gave a k_{rel} of 75.6 for the kinetic resolution of propylene oxide as shown in Scheme 2.[19] However, for other, simpler, Co(III)(salen)-based catalysts, k_{rel}'s of 1.1−11.2 were more typical.[18]

ability of Co(salen) complexes to catalyze other reactions of epoxides including polycarbonate formation[21] and hydrolytic kinetic resolution[11] can result in formation of multiple products and low yields or require the use of expensive co-catalysts to suppress unwanted reactions. Therefore, in view of the mechanistic similarities of hydrolytic kinetic resolution using Co(III)(salen) complexes[13] and cyclic carbonate synthesis using complex **3a**, which both involve two metal(salen) units, coordination of the epoxide to one of the metals, and nucleophilic ring-opening of the coordinated epoxide, we decided to investigate the use of aluminum(salen) complexes as catalysts for nonracemic cyclic carbonate synthesis in more detail. Since aluminum(salen) complexes do not catalyze polycarbonate synthesis or epoxide hydrolysis, a successful kinetic resolution using an aluminum based catalyst was expected to have fewer side reactions than the corresponding cobalt-based catalysts.

We first sought to confirm previous work that aluminum-(salen) catalysts were not able to carry out a kinetic resolution of epoxide **2c**. Bimetallic aluminum(salen) complex **3a** and monometallic aluminum(salen) complexes **3b−d** (Figure 2)
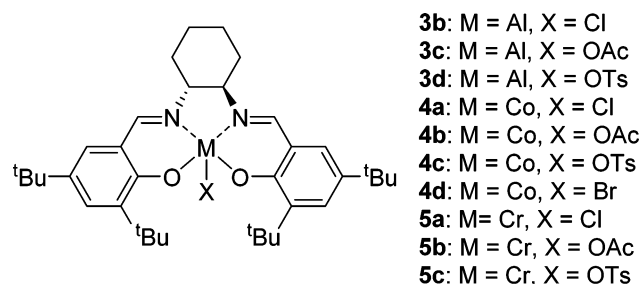
3b: M = Al, X = Cl
3c: M = Al, X = OAc
3d: M = Al, X = OTs
4a: M = Co, X = Cl
4b: M = Co, X = OAc
4c: M = Co, X = OTs
4d: M = Co, X = Br
5a: M = Cr, X = Cl
5b: M = Cr, X = OAc
5c: M = Cr, X = OTs

Figure 2. Structures of monometallic metal(salen) catalysts.

Scheme 2. Cobalt(salen) Complex 4a Catalyzed Synthesis of Enantiomerically Enriched Cyclic Carbonates

0.05 mol % **4a**,
25 mol% PPN-DNP
-25 °C, 8.2 atm CO$_2$,12 h

10 % conversion
97.1 % ee

$[Ph_3P=N=PPh_3]^+$

PPN-DNP

4a: X = 2,4,-dinitrophenoxy

were synthesized and used with tetrabutylammonium bromide to catalyze the conversion of epoxide **2c** into cyclic carbonate **1c**. For a kinetic resolution, the enantiomeric excess of the cyclic carbonate product is dependent on the extent of conversion, so k_{rel} values were calculated and are given in Table 1 (entries 1−4). This screening of chiral aluminum-(salen) complexes with styrene oxide showed only very low levels of enantioselectivity, if any, which is in agreement with previous work.[7a] Hydrolytic kinetic resolution of epoxides using Co(III)(salen) complexes is known to be essentially independent of the size of the epoxide substrate.[11] To investigate if this was also the case for asymmetric cyclic carbonate synthesis, the substrate was changed to phenyl glycidyl ether **2d** or N-(2,3-epoxypropyl)diphenylamine[20] **2e**, and the k_{rel} values increased significantly (Table 1, entries 5−20). Clearly, in contrast to hydrolytic kinetic resolution, the effectiveness of this kinetic resolution is dependent on the epoxide structure. In addition, lowering the reaction temperature improved the enantioselectivity, but necessitated longer reaction times to compensate for slower rates of cyclic carbonate formation (Table 1, entries 9−12 and 17−20).

The influence of the co-catalyst on the rate and enantioselectivity of the kinetic resolution of epoxide **2d** was investigated using catalyst **3a**, and the results are shown in Table 1, entries 21−26. The results with tetraalkylammonium salts showed that the rate of reaction increased as the nucleophilicity and leaving group ability of the halide increased (F < Cl < Br < I). However, tetrabutylammonium iodide gave virtually racemic product (Table 1, entry 23). In view of the

Despite the impressive k_{rel} values that can be obtained, Co(salen) complexes are less than ideal catalysts for the synthesis of nonracemic cyclic carbonates. The reactions usually require low temperatures and/or high pressures of carbon dioxide (with a few notable exceptions at 1 bar carbon dioxide pressure and temperatures around ambient[18b,m,19]), and the

Table 1. Cyclic Carbonate Synthesis Catalyzed by Aluminum and Cobalt(III)(salen) Complexes[a]

entry	catalyst	co-catalyst	epoxide	time (h)	temp (°C)	conv (%)	cyclic carbonate er[b]	k_{rel}[c]
1	3a	Bu$_4$NBr	2c	3	25	21	48:52	1.1
2	3b	Bu$_4$NBr	2c	3	25	21	47:53	1.1
3	3c	Bu$_4$NBr	2c	3	25	28	50:50	1.0
4	3d	Bu$_4$NBr	2c	3	25	7	47:53	1.1
5	3a	Bu$_4$NBr	2d	1	25	34	40:60	1.7
6	3b	Bu$_4$NBr	2d	1	25	35	42:58	1.5
7	3c	Bu$_4$NBr	2d	1	25	41	39:61	1.8
8	3d	Bu$_4$NBr	2d	1	25	4	32:68	2.2
9	3a	Bu$_4$NBr	2d	42	0	25	25:75	3.6
10	3b	Bu$_4$NBr	2d	24	0	17	25:75	3.3
11	3c	Bu$_4$NBr	2d	24	0	36	23:77	4.3
12	3d	Bu$_4$NBr	2d	72	0	8	21:78	3.8
13	3a	Bu$_4$NBr	2e	4	25	59	27:73	5.3
14	3b	Bu$_4$NBr	2e	4	25	36	16:84	7.7
15	3c	Bu$_4$NBr	2e	4	25	56	23:77	6.4
16	3d	Bu$_4$NBr	2e	18	25	19	21:79	4.3
17	3a	Bu$_4$NBr	2e	24	0	3	8:92	11.6
18	3b	Bu$_4$NBr	2e	24	0	11	8:92	13.7
19	3c	Bu$_4$NBr	2e	24	0	15	7:93	15.4
20	3d	Bu$_4$NBr	2e	64	0	14	10:90	10.7
21	3a	Bu$_4$NF	2d	24	25	11	42:58	1.1
22	3a	Bu$_4$NCl	2d	6	25	20	33:67	2.2
23	3a	Bu$_4$NI	2d	3	25	48	49:51	1.1
24	3a	GndCl[d]	2d	24	25	2		
25	3a	PPN$^+$Cl^{-e}	2d	6	25	32	36:64	2.0
26	3a	DMAP	2d	24	25	10	42:58	1.4
27	4b	Bu$_4$NBr	2e	24	0	8	32:68	2.2
28	4c	Bu$_4$NBr	2e	24	0	21	33:67	2.3
29	4d	Bu$_4$NBr	2e	64	0	17	39:61	1.6
30	4e	Bu$_4$NBr	2e	24	0	34	41:59	1.6

[a]Reactions were carried out using 2.5 mol % of catalyst and 2.5 mol % of co-catalyst under solvent-free conditions with 1 bar of CO$_2$ pressure. [b]er values for the cyclic carbonate were obtained by chiral HPLC using a Chiralcel OD column (for 1c and 1d) or a Chiracel IA column (for 1e) and correspond to the area under the first peak/area under second peak. The epoxide enantiomers did not give separate peaks under the HPLC conditions. [c]k_{rel} is calculated as $(\ln[1 - c(1 + ee)])/(\ln[1 - c(1 - ee)])$ where c = conversion and ee = enantiomeric excess. [d]GndCl: Guanidinium chloride. [e]PPN$^+$Cl$^-$: bis(triphenylphosphine)iminium chloride.

promising selectivity factor obtained using tetrabutylammonium chloride (Table 1, entry 22), two other chloride salts were investigated, but guanidinium chloride gave a very low conversion (Table 1, entry 24), and while bis-(triphenylphosphine)iminium chloride (PPN$^+$Cl$^-$) increased the conversion, it did not increase the selectivity factor (Table 1, entry 25). Finally, the use of DMAP as a co-catalyst was investigated (Table 1, entry 26), but the reaction was found to be very slow. Notably, all of the results given in Table 1 were obtained at just 1 bar of carbon dioxide pressure. While bimetallic complex 3a has previously been shown to be more catalytically active than monometallic aluminum(salen) complexes,[7] monometallic complexes 3b and 3c appear to be more enantioselective than bimetallic complex 3a (Table 1, entries 5−20).

Since similar cobalt(salen) catalysts have been reported to kinetically resolve terminal epoxides via cyclic carbonate formation,[18,19] as well as via Jacobsen's hydrolytic kinetic resolution,[11] cobalt(III)(salen) complexes 4a−d were synthesized and studied in the conversion of N-(2,3-epoxypropyl)-diphenylamine 2e to cyclic carbonate 1e to provide a comparison with the results obtained using aluminum(salen) complexes 3a−d. The structure of complex 4d was confirmed by X-ray crystallography (Figure 3).[22] When using cobalt(III)-
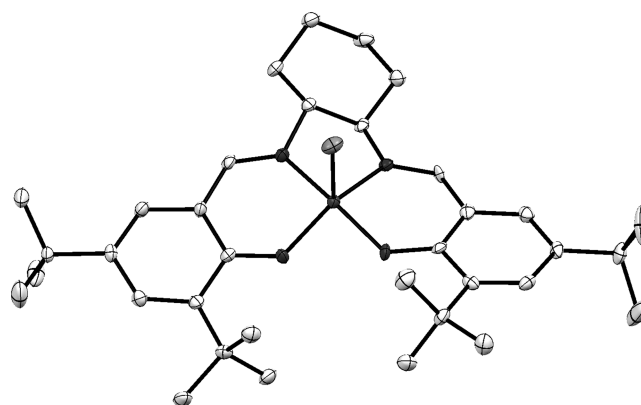

Figure 3. ORTEP plot of Co(salen)Br 4d with ellipsoids drawn at 50% probability.

(salen) catalysts, it was necessary to take care to exclude moisture from the reaction mixture as catalyzed epoxide hydrolysis was found to be faster than cyclic carbonate synthesis. While the aluminum(salen) complexes could produce k_{rel} values in excess of 10 with N-(2,3-epoxypropyl)-diphenylamine 2e as substrate (Table 1, entries 17−20), the cobalt(III)(salen) complexes gave much lower k_{rel} values at the

same temperature and catalyst loading (Table 1, entries 27−30), at least when using epoxide **2e** as substrate.

The enantiomeric ratio of cyclic carbonates **1c−e** was determined by chiral HPLC on a Chiralcel OD or IA column, and in each case, the second eluting enantiomer was found to be the major enantiomer. For cyclic carbonates **1c,d** this was shown to correspond to the (S)-enantiomer by carrying out reactions between commercially available, enantiomerically pure epoxides **2c,d** and carbon dioxide catalyzed by aluminum complex **3a** under reaction conditions which are known to result in retention of epoxide stereochemistry.[7,9]

Catalysts **4a−c** were active only in the presence of tetrabutylammonium bromide, which raised the possibility that they may just be precatalysts for complex **4d** formed in situ by ligand exchange. However, complex **4d** was also active only in the presence of tetrabutylammonium bromide, suggesting that the tetrabutylammonium bromide plays a different role in the reaction mechanism.

Chromium(salen) complexes **5a** to **5c** were also investigated as catalysts for (phenoxymethyl)ethylene carbonate **1d** synthesis since chromium(salen) complexes have been reported to be highly enantioselective in the ring-opening of terminal epoxides using trimethylsilyl azide.[12] Initial testing with tetrabutylammonium bromide or 4-(dimethylamino)pyridine as co-catalysts showed that catalysts **5a** and **5c** were the most enantioselective (Table 2, entries 3, 5, and 11−14), though

Table 2. Cyclic Carbonate Synthesis Catalyzed by Chromium(salen) Complexes in the Presence of Various Co-catalysts[a]

entry	catalyst	co-catalyst	epoxide	time (h)	conv (%)	cyclic carbonate er	k_{rel}
1	5a	NBu₄F	2d	24	63	43:57	1.6
2	5a	NBu₄Cl	2d	24	89	44:56	2.9
3	5a	NBu₄Br	2d	6	62	49:51	1.1
4	5a	NBu₄I	2d	6	43	49:52	1.1
5	5a	DMAP[b]	2d	24	62	39:62	2.2
6	5a	GndCl[c]	2d	24	17	45:55	1.3
7	5a	PPN⁺Cl⁻[d]	2d	6	17	37:63	1.8
8	5a	PPN⁺Cl⁻	2d	24	84	42:58	3.1
9[e]	5a	PPN⁺Cl⁻	2d	3	17	29:71	2.7
10	5a	PPN⁺Cl⁻	2e	3	21	14:86	7.3
11	5b	NBu₄Br	2d	6	78	49:51	1.1
12	5b	DMAP[b]	2d	24	52	46:55	1.3
13	5c	NBu₄Br	2d	24	23	37:63	1.9
14	5c	DMAP[b]	2d	24	6	53:47	1.1
15	5c	PPN⁺Cl⁻	2d	24	22	37:63	1.7

[a]Reactions were carried out using 2.5 mol % of catalyst and 2.5 mol % of tetrabutylammonium bromide under solvent-free conditions at 25 °C. [b]DMAP: 4-(dimethylamino)pyridine. [c]GndCl: guanidinium chloride. [d]PPN⁺Cl⁻: bis(triphenylphosphine)iminium chloride. [e]5.0 mol % of catalyst and co-catalyst loading was used.

only low k_{rel} values were observed (1.1−2.2). Screening of other tetrabutylammonium halide co−catalysts with chromium complex **5a** (Table 2, entries 1−4) revealed that tetrabutylammonium chloride gave the most enantioselective catalyst system (k_{rel} 2.9), though this was combined with a reduction in the reaction rate compared to reactions carried out with tetrabutylammonium bromide or iodide as the co-catalysts. Unusually, tetrabutylammonium fluoride also gave a catalyst

system which was moderately active and moderately enantioselective.

Having determined chloride to be the optimal halide within the co-catalyst, the effect of changing the cation was investigated. Guanidinium chloride (Table 2, entry 6) was both less reactive and less enantioselective than tetrabutylammonium chloride, but bis(triphenylphosphine)iminium chloride (Table 2, entries 7, 8, and 15) gave a small increase in the k_{rel} to 3.1 and afforded results comparable to those obtained using the aluminum(salen) catalysts with tetrabutylammonium bromide, though at increased cost. Doubling the catalyst loading doubled the reaction rate and increased the k_{rel} values (Table 2, entries 7 vs 9). These effects may be due to the reaction being bimolecular in Cr(salen) complex as is known to be the case for other metal(salen)-catalyzed kinetic resolutions of epoxides.[12,13] Thus, increasing the concentration of catalyst will facilitate this bimolecular pathway relative to slower and less enantioselective reaction pathways catalyzed by a single metal(salen) complex. The same bimetallic transition states resulting from cooperative catalysis can be obtained from monometallic aluminum(salen) complexes **3b−d** even though the complexes are themselves monometallic.

The optimized system of catalyst **5a** in the presence of PPN⁺Cl⁻ was then used in the conversion of *N*-(2,3-epoxypropyl)diphenylamine **2e** to cyclic carbonate **1e** (Table 2, entry 10). Once again, a higher enantioselectivity was observed for substrate **2e** than for phenyl glycidyl ether **2d**, though the k_{rel} value (7.3) was significantly lower than that obtained for the same reaction catalyzed by aluminum(salen) complexes (10.7−15.4).

Of the results given in Table 1, those in entries 13 and 15 appear optimal in terms of giving around 50% conversion of racemic epoxide in 4 h at 25 °C while also giving reasonable k_{rel} values for the kinetic resolution. The reaction shown in entry 13 was then studied in more detail by carrying out the reaction in duplicate for 8 h and removing samples for HPLC analysis to study the variation of cyclic carbonate enantiomeric excess with reaction conversion. Figure 4 shows that an excellent fit of the experimental data to the theoretical curve is obtained for both data sets.

It appears that kinetic resolution during cyclic carbonate formation is mediated by interactions between the catalyst and
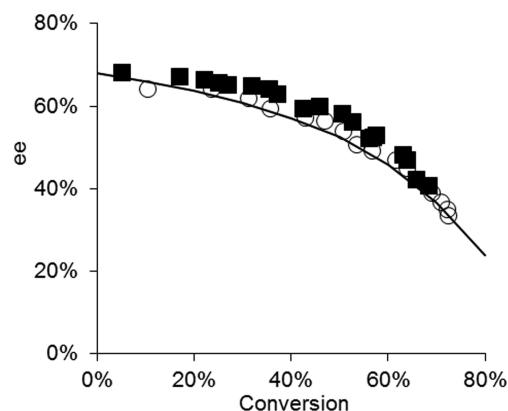

Figure 4. Observed ee of 4-((N,N-diphenylamino)methyl)-1,3-dioxolan-2-one against conversion for two separate runs (blue and red). The theoretical ee against conversion for a catalyst with k_{rel} 5.27 obtained by plotting 5.27 = $(\ln(1 - c(1 + ee)))/(\ln(1 - c(1 - ee)))$ is shown by the solid line.

the epoxide side chain. The R groups of phenyl glycidyl ether **2d** and *N*-(2,3-epoxypropyl)diphenylamine **2e** project further out from the oxirane ring, thus facilitating discrimination between enantiomers of the substrates.

In conclusion, the first aluminum-based catalysts capable of carrying out the kinetic resolution of epoxides during cyclic carbonate synthesis have been developed. The aluminum-(salen) complexes afforded k_{rel} values which are higher than the corresponding cobalt and chromium complexes derived from the same ligand. The kinetic resolution is a 100% atom-economical process that can be carried out at 0 °C and 1 atm of carbon dioxide pressure, thus reducing the environmental impact of the process compared to previously reported catalyst systems for the same reaction.[18,19] Aluminum is also the most abundant metal in the Earth's crust and is relatively nontoxic compared to cobalt and chromium.

Mechanistically, although there appears to be a close similarity between cyclic carbonate synthesis and hydrolytic kinetic resolution, the reactions display very different substrate tolerances. Thus, whereas hydrolytic kinetic resolution is virtually independent of the structure of the terminal epoxide, kinetic resolution during cyclic carbonate synthesis is very dependent on the nature of the epoxide side chain. This may indicate that the reactions have different stereodetermining steps.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org/.The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00235.

　　Experimental details (PDF)
　　X-ray data for compound **4d** (CIF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: michael.north@york.ac.uk.

Notes
The authors declare no competing financial interest.

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