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Chiral (salen)Co^{III} catalyst for the synthesis of cyclic carbonates†

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A catalyst system comprised of a Co^{III}(salen) complex and a Lewis base is investigated for the reaction of CO$_2$ and a variety of epoxides to form cyclic carbonates. Application of this catalyst system in the kinetic resolution of propylene oxide is also discussed.

The development of synthetic processes which incorporate CO$_2$ remains a very important challenge, both in the context of carbon-management and from a practical standpoint: CO$_2$ is an ideal C$_1$ feedstock in that it is safe, inexpensive and abundant. Although the coupling of CO$_2$ and epoxides to form cyclic carbonates and polycarbonates has been known for over 50 years,[1] the past decade has seen a resurgence of interest in the development of well-defined and selective catalyst systems for these reactions.[2]

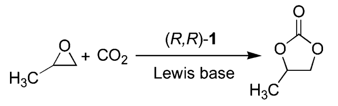
Recently we reported a highly efficient Cr^{III}(salen)/DMAP catalyst system for the coupling of CO$_2$ and epoxides to provide cyclic carbonate in high yield under mild reaction conditions.[2b] Jacobsen *et al.* have demonstrated that in addition to Cr^{III}(salen) complexes, Co^{III}(salen) complexes also function as catalysts for the ring-opening of epoxides with a variety of nucleophiles.[3] Thus we began to explore the possibility of employing Co^{III} macrocycles as catalysts for the coupling of CO$_2$ and epoxides.[4] Coates and coworkers' recent communication[5] regarding the use of Co^{III}(salen) complexes for polycarbonate synthesis prompted us to disclose our results in evaluating these complexes as catalysts, in conjunction with a Lewis base (LB), for the reaction of CO$_2$ and epoxides to yield cyclic carbonates.

The Co^{III}(salen) **1**/DMAP catalyst system was found to be highly active for the reaction of CO$_2$ and propylene oxide to yield propylene carbonate (eqn. 1), with a turn-over frequency (TOF) that is comparable to the most active catalyst reported to date (Table 1, entry 1).[2f] We found **1** to be much more active than the analogous Co^{II}(salen) complex which demonstrated only limited activity (Table 1, entry 2).[6] The LB co-catalyst is required for high activity; in its absence catalyst **1** yielded only a trace amount of the product (Table 1, entry 3). Several LBs were tested as co-catalyst for reaction 1, with an increase in Lewis basicity resulting in a corresponding increase in activity (Table 1, entries 1, 4–6). The number of equivalents of DMAP, the best LB tested, were varied relative to catalyst **1** and found to be optimal at 2, the TOF was halved when employing 1 equiv. and decreased steadily above 2 equiv. (Table 1, entries 1, 7–9).

Table 1 Activity of the **1**/Lewis base catalyst system in the coupling of CO$_2$ and propylene oxide[a]

Entry	Lewis base	LB (# equiv.)	TON[b]	TOF (h^{-1})[c]
1	DMAP	2	400	1200
2[d]	DMAP	2	147	16
3	None	0	20	0.5
4	Pyridine	2	452	25
5	*N*-Me-imidazole	2	422	506
6	Triethylamine	2	395	99
7	DMAP	1	452	603
8	DMAP	4	497	993
9	DMAP	8	464	697

[a] Reaction conditions: catalyst **1** (0.066 mol%), propylene oxide (3.5 mL, 1500 equiv.), CO$_2$ (300 psig), CH$_2$Cl$_2$ (0.5 mL), 100 °C. [b] mol of propylene carbonate produced per mol of catalyst. [c] mol of propylene carbonate produced per mol of catalyst per hour. [d] Co^{II}(salen) as catalyst.



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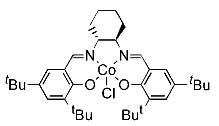
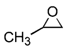
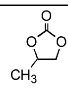
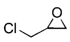
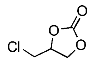
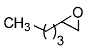
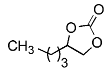
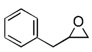
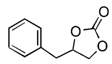
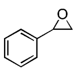
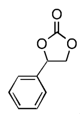
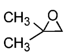
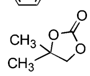
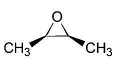
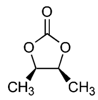


(*R*,*R*)-**1**

The **1**/DMAP catalyst system was determined to effectively convert a variety of monosubstituted terminal epoxides to the corresponding cyclic carbonates in near quantitative yield (Table 2). This includes epoxides which possess aliphatic, aromatic, electron-withdrawing and -donating substituents. The catalyst system was also active towards the conversion of a 1,1-disubstituted epoxide, though as anticipated this required longer reaction times. An internal epoxide, diastereomerically pure *cis*-2,3-epoxybutane, was also employed as a substrate and was successfully converted to the corresponding cyclic carbonate with an overall retention of configuration (93 : 7 *cis* : *trans*, Table 2 footnote *d*). In the presence of the **1**/DMAP catalyst system, reaction of enantiomerically pure (*R*)-propylene oxide with CO$_2$ yielded enantiomerically pure propylene carbonate with complete retention of the original stereochemistry.

Table 2 Substrate scope for the **1**/DMAP catalyst system[a]

Substrate	Time (h)	Product	Yield[b]
	1.5		100%
	1		100%[c]
	1.5		95%
	1.5		100%
	1.5		98%
	16		94%
	12		95%[d,e]

[a] Reaction conditions: **1** (1 mol%), DMAP (2 mol%), epoxide (1 mL, 100 equiv.), CO$_2$ (300 psig), CH$_2$Cl$_2$ (0.5 mL), 100 °C. [b] Yields were determined by comparing the ratio of product to substrate in the ^{1}H NMR spectrum of an aliquot of the crude reaction mixture. [c] **1** (0.4 mol%). [d] The substrate was diastereomerically pure. [e] Product *cis* : *trans* ratio (93 : 7).

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† Electronic supplementary information (ESI) available: general experimental procedures and analytical data for new compounds. See http://www.rsc.org/suppdata/cc/b4/b401543f/

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The formation of enantiomerically pure cyclic carbonates from enantiomerically pure epoxides and CO_2 has been demonstrated.[2b,7] However, employing chiral Co^{III}(salen) complexes as catalysts offers the potential for kinetic resolution of racemic epoxides, providing both enantiomerically enriched epoxide and cyclic carbonate as products. We investigated this possibility and the initial results for the kinetic resolution of propylene oxide are presented in Table 3. Under the previously optimized reaction conditions, the **1**/DMAP catalyst system demonstrated a selectivity factor,[8] s, of 1.8 (Table 3, entry 2). When the corresponding Co^{II}(salen) complex was employed as catalyst a selectivity of 1.1 was attained (Table 3, entry 1).

Decreasing the temperature had a notable effect, increasing the selectivity to 3 at r.t. (Table 3, entries 3 and 4). However, at these lower temperatures the TOF decreased and a mixture of propylene carbonate and poly(propylene carbonate) was formed. Heating this product mixture *in vacuo* resulted in complete degradation of the polymer to the cyclic carbonate product[9] without a change in enantioselectivity.[10]

To further improve enantioselectivity, (*R*)-(+)-4-dimethylaminopyridinyl(pentaphenylcyclopentadienyl)iron, DMAP*, a planar chiral DMAP which has recently been successfully employed as a catalyst in a number of enantioselective reactions,[11] was investigated as a co-catalyst. The use of DMAP* resulted in an increase in selectivity to 4.8, as well as a 10-fold increase in TOF at r.t. This increase in activity allowed us to investigate the reaction at 3 °C which improved the selectivity further to 5.6 (Table 3, entries 5 and 6).

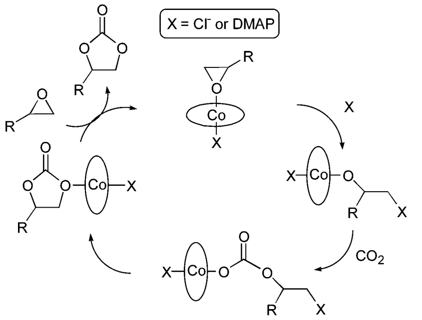
Interestingly, changing the isomer of catalyst to (*S,S*)-Co^{III}(salen) while using the same isomer of DMAP* did not change the TOF or selectivity factor but merely provided the opposite enantiomer of product. Thus, it appears that the chiral nature of the co-catalyst is not a significant contributor to the overall enantioselectivity. To test this conjecture, we employed *N,N*-4-dimethylaminoquinoline (DMAQ) as a co-catalyst and indeed obtained a selectivity similar to that obtained with the DMAP* co-catalyst, albeit with a slight decrease in rate, supporting our hypothesis that the chirality of the LB does not contribute significantly to the improved selectivity. *N,N*-9-Dimethylaminoacridine (DMAA) also yields a similar selectivity but a slower rate (Table 3, *cf.* entries 5, 7–8), suggesting that the steric bulk and the electron donating ability of the LB are the important factors in determining activity and selectivity.

The possible role of the LB co-catalyst in dual-site LA/LB (LA = Lewis acid) catalyst systems for the coupling of CO_2 and epoxides has been investigated.[2e,12] These reports have proposed that the LB acts as a nucleophile to ring-open the LA-activated epoxide. In our system, the LB may also serve an important role in facilitating the insertion of CO_2 into the ring-opened intermediate (Scheme 1). This is supported by the observation that in the absence of a LB, Co^{III}(salen) complexes are inactive for CO_2/epoxide coupling at pressures below 600 psig, perhaps limited by the CO_2 insertion step.[5] However, in our work, the presence of a LB allows for the coupling of CO_2/epoxides at 300 psig of CO_2. Thus, the LB seems to have enabled the rate-limiting CO_2 insertion step. That the LB may have more than one role also explains why 2 equiv. of DMAP are optimal. One equiv. may coordinate to the LA, facilitating CO_2 insertion leaving the other free to act as a nucleophile to ring open the epoxide. Excess DMAP can inhibit activation of the epoxide substrate by competing for coordination to the Co complex and therefore leads to a decrease in TOF (Table 1, *cf.* entries 1, 8–9).

Table 3 Enantioselective reaction of CO_2 and propylene oxide[a]

Entry	Lewis base	Temp. (°C)	Time (h)	TOF (h^{-1})	s[c]
1[b]	DMAP	100	9	16	1.1
2	DMAP	100	0.33	1200	1.8
3	DMAP	50	8	65	2.8
4	DMAP	r.t.	48	9	3.0
5	DMAP*	r.t.	4.5	115	4.8
6	DMAP*	3	50	10	5.6
7	DMAQ	r.t.	15	47	4.6
8	DMAA	r.t.	37	13	4.7

[a] Reaction conditions: catalyst **1** (0.066 mol%), Lewis base (0.132 mol%), propylene oxide (3.5 mL, 1500 equiv.), CO_2 (300 psig), CH_2Cl_2 (0.5 mL). [b] Co^{II}(salen) as catalyst. [c] See ref. 8.



Scheme 1 Proposed mechanism for CO_2/epoxide coupling.

In conclusion, we have demonstrated that Co^{III}(salen) complexes, in conjunction with a LB co-catalyst, are effective and versatile catalysts for the coupling of CO_2 and epoxides, including mono- and di-substituted terminal epoxides as well as internal epoxides. In addition, initial investigations into the kinetic resolution of epoxides with CO_2 have shown encouraging selectivities. We have demonstrated that the steric bulk and electronic properties of the co-catalyst can play a significant role in determining the system's selectivity in addition to the activity.

Notes and references

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