11498 J. Am. Chem. Soc. 2001, 123, 11498−11499

# Chemical CO$_2$ Fixation: Cr(III) Salen Complexes as Highly Efficient Catalysts for the Coupling of CO$_2$ and Epoxides

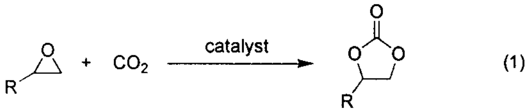
Robert L. Paddock and SonBinh T. Nguyen*

*Department of Chemistry and Institute for*
*Environmental Catalysis, Northwestern University*
*2145 Sheridan Road, Evanston, Illinois 60208-3113*

*Received June 21, 2001*

Carbon dioxide is an attractive C$_1$ building block in organic synthesis as it is highly functional, abundant, inexpensive, nontoxic, and nonflammable. As petroleum reserves are depleted, the development of efficient catalytic processes employing CO$_2$ as a feedstock has become increasingly important as evidenced by the intense research in this area in recent years.[1−3] However, due to the inert nature of CO$_2$, efficient catalytic processes for chemical fixation remain elusive. Thus, in addition to the practical merit, chemical CO$_2$ fixation remains a significant synthetic challenge.

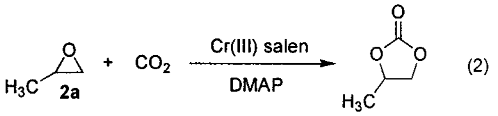
One of the most promising methodologies in this area has been the synthesis of cyclic carbonates via the metal-catalyzed coupling of CO$_2$ and epoxides (eq 1).[4] Cyclic carbonates are valuable as monomers, aprotic polar solvents, pharmaceutical/fine chemical intermediates, and in many biomedical applications.[5,6] In recent decades numerous catalyst systems have been developed for this transformation.[4,7−11] While the advances have been significant, all suffer from either low catalyst stability/reactivity, air sensitivity, the need for co-solvent, or the requirement for high pressures and/or high temperatures. For example, a recently reported catalyst system is a mixed-metal Mg/Al oxide which operates at a reasonable CO$_2$ pressure (5 atm) but requires a substantial amount of solvent (85% v/v DMF) and takes 24 h at 100 °C to convert just 0.28 g of propylene oxide in 88% yield and 92% selectivity, even with a very high catalyst loading of 1.8 g catalyst/ g of substrate.[12]



(1)

Herein, we report a new highly active (salen)Cr(III)-based catalyst system for the synthesis of cyclic carbonates from the coupling of CO$_2$ and terminal epoxides under extremely mild conditions. Kruper et al. have previously reported the use of a Cr(III) porphyrin complex as a catalyst for this reaction.[13,14] Changing the coordination environment around the Cr metal center from a porphyrin to a salen[15] ligand offers several advantages: (1) salens are easily and efficiently synthesized in stark contrast to porphyrins, which are typically obtained in yields of less than 20%,[16] and (2) the modular construction of salens from diamines and salicylaldehydes enables easy tuning of catalyst steric and electronic properties. We were further encouraged by several recent reports of the catalytic nucleophilic ring opening of epoxides using transition metal salen complexes[17−19] and felt that salen complexes could potentially be useful for the electrophilic addition of CO$_2$ to epoxides.

**Table 1.** Effect of Reaction Parameters on the Coupling of CO$_2$ and PO Catalyzed by Complexes **1a**−**d**[a]



(2)

| entry | catalyst | DMAP equiv | CO$_2$ (psig) | temp (°C) | time (h) | total TON[b] | TOF[d] (h$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | **la** | 1 | 100 | 75 | 2 | 323 | 162 |
| 2 | **lb** | 1 | 100 | 75 | 2 | 338 | 169 |
| 3 | **lc** | 1 | 100 | 75 | 2 | 253 | 127 |
| 4 | **1d** | 1 | 100 | 75 | 2 | 507 | 254 |
| 5[c] | **1d** | 1 | 100 | 75 | 2 | 386 | 193 |
| 6 | **none** | 1 | 150 | 75 | 2 | 0 | 0 |
| 7 | **1d** | 0 | 150 | 75 | 2 | 0 | 0 |
| 8 | **1d** | 0.5 | 150 | 75 | 2 | 302 | 151 |
| 9 | **1d** | 1 | 150 | 75 | 2 | 340 | 170 |
| 10 | **1d** | 2 | 150 | 75 | 2 | 458 | 229 |
| 11 | **1d** | 4 | 150 | 75 | 2 | 30 | 15 |
| 12 | **1d** | 1 | 100 | 25 | 14 | 39 | 3 |
| 13 | **1d** | 1 | 100 | 50 | 7 | 179 | 26 |
| 14 | **1d** | 1 | 100 | 100 | 1 | 916 | 916 |

[a] Reaction Conditions: PO (4 mL, 3.32 g, 5.72 × 10$^{-2}$ mol), CH$_2$C1$_2$ (0.5 mL), catalyst (0.075 mol %). [b] Moles of propylene carbonate produced per mole of catalyst. [c] Reaction carried out in neat PO (4 mL). [d] Moles of propylene carbonate produced per mole of catalyst per hour.

Our initial studies showed that **la** successfully catalyzes the coupling of CO$_2$ and propylene oxide (PO) in the presence of a Lewis-basic co-catalyst such as (4-dimethylamino)pyridine (DMAP). No reaction was observed in the absence of DMAP, which is consistent with that observed for the Cr porphyrin-catalyzed reaction.[13] It is important to note that DMAP by itself did not catalyze the reaction. Reaction 2 was run in 1:1 (v/v) mixtures of PO and various co-solvents; however, running the reaction in neat PO gave the best yield of propylene carbonate (PC). This yield could be increased further by the addition of a small amount of CH$_2$Cl$_2$, presumably to help solubilize the catalyst system (Table 1, entries 4−5). Several (salen)Cr(lII) complexes (**la**−**d**) with varying diamine backbones were investigated as catalysts for reaction 2. Complex **1d** exhibited the highest catalytic activity of all the catalysts and is at least twice as active as the racemic *trans* analogue **lc** (Table 1 entries 1−4). We believe this may be due to the more accessible coordination site available in complex **1d**. The *trans-cyclohexyl* salen catalyst **la** and the propylene salen catalyst **1b** are also slightly more active than **1c**. Complex **1d**

---

(1) Leitner, W. *Coord. Chem. Rev.* **1996**, *155*, 257−284.

(2) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH Publishers: New York, 1988.

(3) *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*; Anastas, P. T., Williamson, T. C., Eds.; Oxford University Press: New York, 1998.

(4) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174.

(5) Biggadike, K.; Angell, R. M.; Burgess, C. M.; Farrell, R. M.; Hancock, A. P.; Harker, A. J.; Irving, A. J.; Irving, W. R.; Ioannou, C.; Procopiou, P. A.; Shaw, R. E.; Solanke, Y. E.; Singh, O. M. P.; Snowden, M. A.; Stubbs, R.; Walton, S.; Weston, H. E. *J. Med. Chem.* **2000**, *43*, 19−21.

(6) Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951−976.

(7) Ratzenhofer, M.; Kisch, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *9*, 317−318.

(8) Kihara, N.; Hara, N.; Harando, N. T. *J. Org. Chem.* **1993**, *58*, 6198−6202.

(9) Kawanami, H.; Ikushima, Y. *Chem. Commun.* **2000**, 2089−2090.

(10) Aida, T.; lnoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304−1309.

(11) Kim, H. S.; Kim, J..; Kimee,. J. Lee, B. G.; Jung, O. S.; Jang, H. G.; Kang, S. O. *Angew. Chem., Int. Ed.* **2000**, *39*, 4096−4098.

(12) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526−4527.

(13) Kruper, W. J.; Dellar, D. D. *J. Org. Chem.* **1995**, *60*, 725−727.

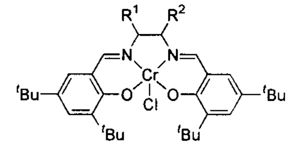
(14) Kruper et al. (ref 13) did not report precise conditions for their reactions. Instead, they gave a range of conditions (i.e., 0.013−0.07 mol % catalyst and 4−10 equiv co-catalyst, 60−100 °C, 730−780 psig, 18−64 h, typically >95% yield).

(15) For the remainder of this article, the term *salen* will be used to describe the general class of bis(salicylaldimine) ligands and complexes.

(16) Shanmugathasan, S.; Edwards, C.; Boyle, R. W. *Tetrahedron* **2000**, *56*, 1025−1046.

10.1021/ja0164677 CCC: $20.00

was then employed to further investigate and optimize the effects of the various reaction parameters on propylene carbonate production.



**1a**: $R^1$and $R^2$ = *trans* -( $CH_2$ )$_4$-
**1b**: $R^1$ = $CH_3$, $R^2$ = H
**1c**: *trans*, $R^1$ = $R^2$ = Ph
**1d**: *meso*, $R^1$ = $R^2$ = Ph

The ratio of DMAP to complex **1d** had a significant effect on the turnover frequency (TOF) (Table 1, entries 6−11). The TOF increased as the number of equiv of DMAP increased, up to two equiv. Increasing the DMAP concentration any further resulted in a loss of activity to the point where the reaction was almost completely shut down when 4 equiv of DMAP were used.

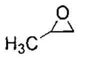
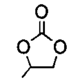
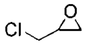
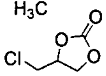
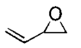
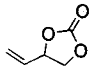
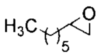
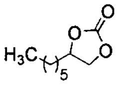
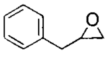
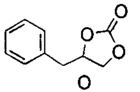
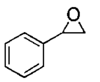
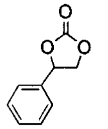
A significant drawback associated with using $CO_2$ as a reagent in organic synthesis is the potential dangers associated with operating at high temperatures and pressures. Thus, we were gratified to discover that our catalyst system can operate very efficiently at low $CO_2$ pressures and temperatures. The highest catalytic activity occurs at 50 psig and is maintained at 80% of this optimum TOF at only 25 psig. Increasing the pressure beyond the optimal level resulted in a dramatic decrease in activity (see Supporting Information), which to the best of our knowledge is the only instance in chemical $CO_2$ fixation where an increase in $CO_2$ pressure causes a decrease in TOF.

Increasing the reaction temperature had a pronounced positive effect on the TOF (Table 1, entries 4 and 12−14). However, we were pleased to discover that the coupling of PO with $CO_2$ could be carried out at a reasonable rate at ambient temperature. The catalyst system exhibits remarkable longevity. The activity does not deteriorate over a period of 50 h, attaining over 8000 turnovers (see Supporting Information).

The catalyst system was found to be applicable to a variety of terminal epoxides,[20] providing the corresponding cyclic carbonates in near quantitative yield and 100% selectivity (Table 2). Both aromatic **2f** and aliphatic **2a**,**d**,**e** epoxides are good substrates for reaction 1. Epichlorohydrin **2b** was found to be the most reactive epoxide, while vinyl epoxide **2c** exhibited the lowest activity of the epoxides surveyed.

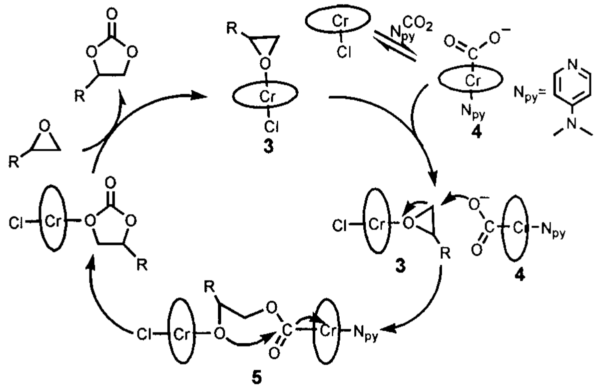
Jacobsen et al. have shown that the nucleophilic ring opening of epoxides catalyzed by Cr(III) salen complexes occurs via catalyst activation of both the electrophilic epoxide and the incoming nucleophile.[21] Previous reports on the synthesis of cyclic carbonate from $CO_2$ and epoxides also suggest the parallel requirement of both Lewis-base-activation of the $CO_2$ and Lewis-acid-activation of the epoxide.[4,12,22] We propose that the starting (salen)CrCI complex in our system fulfills the role of activating the epoxide.[21] The DMAP co-catalyst is necessary for the formation of the more electron-rich Cr(III) center in the (salen)-Cr(III)·DMAP complex **4** which is required to activate $CO_2$. Complex **4** can then attack the activated epoxide complex **3** at the least sterically hindered carbon,[23] leading to the formation of the dimeric intermediate **5** which eventually yields the cyclic carbonate product (Scheme 1). This mechanism can explain the dramatic losses in activity that accompany an increase, beyond an optimal concentration, in either DMAP molar equivalents or $CO_2$ pressure. Both of these situations would lead to an increased formation of **4** at the expense of **3**, thereby reducing the reaction rate. Detailed mechanistic studies will be reported in due course.

**Table 2.** Coupling of $CO_2$ and Various Epoxides Catalyzed by Complex **1d**[a]

| substrate | | temp(°C) | time(h) | product | yield[b] |
|---|---|---|---|---|---|
|  | **2a** | 75 | 1.5 |  | 100% |
|  | **2b** | 75 | 1.5[c] |  | 98% |
|  | **2c** | 85 | 7.5 |  | 94% |
|  | **2d** | 85 | 3.5 |  | 100% |
|  | **2e** | 75 | 6.5 |  | 100% |
|  | **2f** | 85<br>75 | 7<br>12[c] |  | 99%<br>99% |

[a] Reaction conditions: **1d** (27.8 mg, 3.81 × $10^{-5}$ mol), DMAP (4.6 mg, 3.81 × $10^{-5}$ mol), epoxide (3.81 × $10^{-3}$ mol), $CO_2$ (50 psig), $CH_2Cl_2$ (0.5 mL). [b] Yields were determined by comparing the ratio of product to substrate in the $^1$H NMR spectrum of an aliquot of the reaction mixture. [c] Reaction run in neat epoxide.

**Scheme 1.** Proposed Mechanism for Reaction 2



In summary, Cr(III) salen complexes are highly efficient catalysts in the coupling of carbon dioxide with epoxides at mild temperatures and pressures. They represent an air stable, easily synthesized, extremely robust catalyst system which requires no solvent and tolerates multiple substrates. These characteristics make them ideal catalysts for chemical $CO_2$ fixation.

**Acknowledgment.** This work was supported by the EMSI program of the NSF and the DOE (NSF No. CHE-9810378) at the Northwestern University Institute for Environmental Catalysis. S.T.N. is an Alfred P. Sloan Research Fellow. Additional support from the DuPont and Union Carbide Companies and the Packard Foundation are appreciated. We thank Dr. W. Jack Kruper and Professor Kenneth R. Poeppelmeier for helpful discussions.

**Supporting Information Available:** Experimental procedures are available (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0164677

---

(17) Wu, M. H.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 5252−5254.

(18) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277,* 936−938.

(19) Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117,* 5897−5898.

(20) Cyclic epoxides such as cyclohexene oxide yield the corresponding polycarbonates.

(21) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118,* 10924−10925.

(22) Yano, T.; Matsui, H.; Koike, T.; Ishiguro, H.; Fujihara, H.; Yoshihara. M.; Maeshima, T. *Chem. Commun.* **1997**, 1129−1130.

(23) The coupling of chirally pure (*R*)-(+)propylene oxide with $CO_2$ using **1d** results in pure (*R*)-(+)propylene carbonate, a complete retention of stereochemistry that is consistent with a ring-opening attack at the least hindered carbon.