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Letters

Co(III) porphyrin/DMAP: an efficient catalyst system for the synthesis of cyclic carbonates from CO_2 and epoxides

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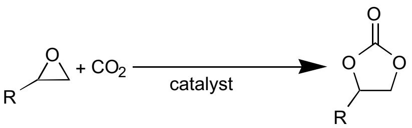
Abstract—CoTPP(Cl)/DMAP was found to be a highly active catalyst system for the chemical fixation of CO_2 via reaction with epoxides. The corresponding cyclic carbonate products are produced in high yield and selectivity for a variety of terminal mono and disubstituted epoxides. 1,2-Disubstituted internal epoxides were also investigated as substrates and found to react with very high stereospecificity.

The reaction of CO_2 with epoxides to yield cyclic carbonates (Eq. 1) has garnered much attention in recent years.[1,2] Cyclic carbonates are valuable products, finding use as organic synthetic intermediates, aprotic polar solvents, precursors for biomedical applications, and as raw materials for engineering plastics.[1–4] In addition, chemical CO_2 fixation is a challenging and important synthetic goal as CO_2 is an inexpensive and abundant C_1 feedstock and therefore any efficient reactions using CO_2 as a reagent would have positive ramifications on efforts toward carbon management.[5]



(1)

A number of catalysts have been reported for reaction 1, including alkali metal salts, ammonium salts, ionic liquids, metal oxides, transition metal and main group complexes.[6–17] However, these usually suffer from drawbacks such as low catalyst activity/selectivity, air sensitivity, and the requirement for harsh reaction conditions. Further, the catalysts must generally be two-component systems comprising of both a Lewis acid and Lewis base to achieve an adequate rate for coupling of CO_2 and epoxides.

We recently reported the use of a Cr^{III} salen/DMAP catalyst system for reaction 1.[18] Similar to the aforementioned reports, the presence of both a Lewis acidic center (the Cr^{III} salen complex) and a Lewis base (DMAP) is necessary for high efficiency and selectivity. During the course of that work we began to investigate the effectiveness of other metal centers to function as the Lewis acidic component. We were pleased to discover that a Co^{III} porphyrin complex, in conjunction with an organic Lewis base, is an excellent catalyst for reaction 1. Herein, we disclose our results for the optimization and application of this catalyst system to cyclic carbonate synthesis.[19]

We chose to utilize a porphyrin complex based on the success that Kruper et al. had when they employed a Cr porphyrin complex as catalyst for reaction 1.[11] Commercially available Co^{II} tetraphenylporphyrin (CoTPP) was initially tested as a catalyst for the coupling of propylene oxide (PO) and CO_2. Though the turn-over number (TON) was limited (Table 1, entry 1), we were encouraged that the Co^{II} complex did exhibit some catalytic activity in the presence of a Lewis base. This prompted us to investigate the possibility of using a more Lewis acidic metal center, which might better activate the epoxide (vide infra). Co^{II}TPP was oxidized

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Keywords: Cyclic carbonates; Co(III) porphyrin; CO_2 fixation; Epoxides.

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Table 1. Activity of Co(TPP) catalysts/Lewis base co-catalysts in the coupling reaction of CO_2 and propylene oxide[a]

Entry	Catalyst/co-catalyst	Time (h)	TON[b]	TOF[c] (h^{-1})
1	CoTPP/DMAP	2.25	36	16
2	CoTPP(Cl)/DMAP	1.33	1102	826
3	CoTPP(Cl)/pyridine	8.5	71	8
4	CoTPP(Cl)/pyridine *N*-oxide	5	0	0
5	CoTPP(Cl)/1-methylimidazole	20.5	1643	80
6	CoTPP(Cl)/triethylamine	22.5	1947	85
7	CoTPP(Cl)/$OPCy_3$	6	0	0
8	CoTPP(Cl)/PPh_3	20	182	9

[a] Reaction conditions: catalyst (2.76×10^{-5} mol, 0.038 mol%), co-catalyst (2 equiv), propylene oxide (5 mL, 2600 equiv), CO_2 (250 psig), CH_2Cl_2 (1.0 mL), 120 °C.[21]

[b] Moles of propylene carbonate produced per mole of catalyst.

[c] Moles of propylene carbonate produced per mole of catalyst per hour.

to the more electrophilic Co^{III}TPP(Cl) complex,[20] which was then tested and found to be an extremely effective catalyst in the presence of a Lewis base co-catalyst (Table 1, entry 2), exhibiting activities that are over 50 times those observed for Co^{II}TPP.

Several other Lewis bases were investigated as possible co-catalysts for Co^{III}TPP(Cl) (Table 1, entries 2–8).[22] DMAP gave superior activity in comparison to all other co-catalysts tested, which we attribute to its high Lewis basicity. Less Lewis basic co-catalysts tend to give diminishing turn-over frequencies (TOF). However, if the Lewis base is sterically bulky, a decrease in TOF can also be observed (cf. entries 2, 5, 6, 8 in Table 1).

Satisfied with our choice of co-catalyst, we set out to further optimize other reaction parameters. CO_2 pressure was found to strongly influence catalyst activity (Fig. 1). The TOF increases significantly with an increase in pressure up to 200 psig and then drops off very slightly at pressures above 300 psig. A similar correlation between catalyst activity and CO_2 pressure was also exhibited by our Cr^{III} salen catalyst although in that case optimal catalyst activity was observed at a lower pressure (50 psig) and the decline in activity was much sharper when the pressure was increased above 50 psig.[18]

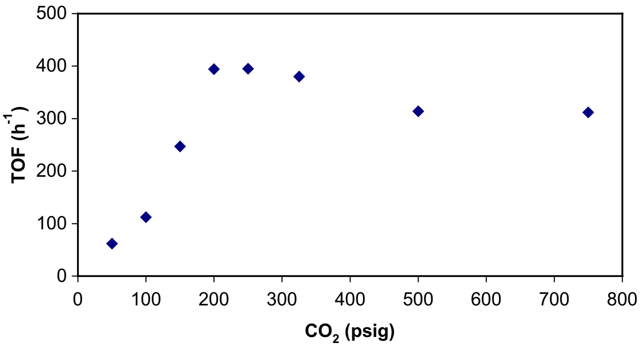


Figure 1. Catalyst TOF for the Co(TPP)Cl/DMAP system as a function of CO_2 pressure. Reaction conditions: CoTPP(Cl) (2.76×10^{-5} mol, 0.038 mol%), DMAP (2 equiv), propylene oxide (5 mL, 2600 equiv), CH_2Cl_2 (1.0 mL), 120 °C.

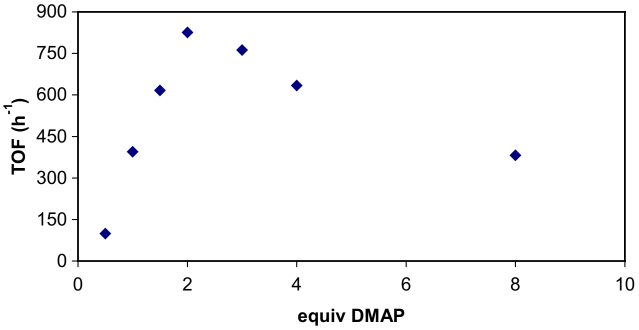
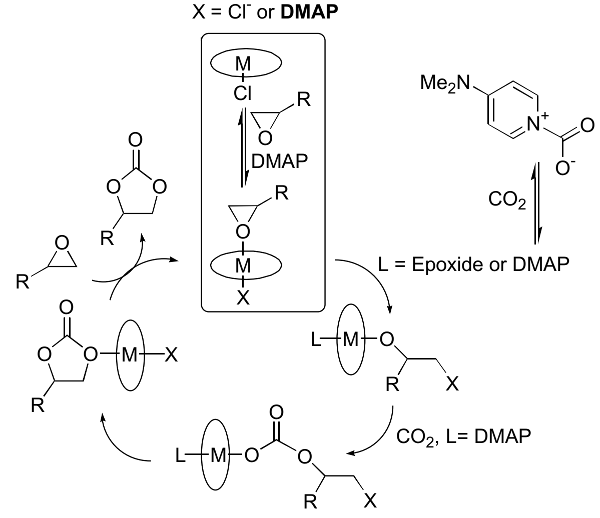


Figure 2. Catalyst TOF for the Co(TPP)Cl/DMAP system as a function of DMAP equivalents. Reaction conditions: CoTPP(Cl) (2.76×10^{-5} mol, 0.038 mol%), propylene oxide (5 mL, 2600 equiv), CO_2 (250 psig), CH_2Cl_2 (1.0 mL), 120 °C.

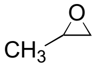
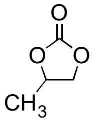
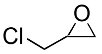
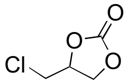
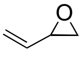
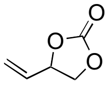
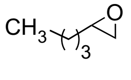
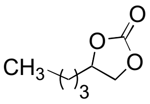
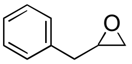
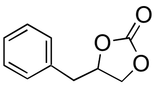
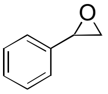
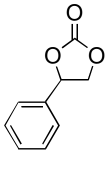
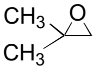
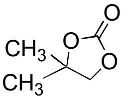
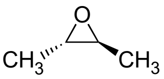
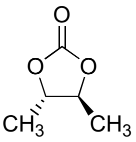
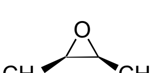
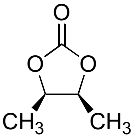
The number of equivalents of co-catalyst employed was also found to be quite important. While the presence of DMAP is critical for high activity and the TOF dramatically increased upon going from 0.5 to 2 equiv of DMAP (Fig. 2), further addition of DMAP past 2 equiv results in a decrease of the TOF.

The above results can be explained by considering a mechanism for this reaction that is similar to that reported by Inoue et al. for the synthesis of ethylene carbonate from ethylene oxide and CO_2 using an Al porphyrin/1-methylimidazole catalyst system.[23] In this mechanism (Scheme 1), the epoxide must first be activated via binding to a coordinatively unsaturated Lewis acidic metal center followed by nucleophilic ring-open-



Scheme 1. A proposed mechanism for the coupling of CO_2 and epoxides by a Lewis acid/DMAP catalyst system.

Table 2. Substrate scope for the Co(TPP)Cl/DMAP system[a]

Substrate	Time (h)	Product	Yield (%)[b]
	1		99
	1		100
	2		92
	2		99
	3		100
	4		97
	12		97[c]
	20		93[c,d]
	9		99[e]

[a] Reaction conditions: CoTPP(Cl) (0.4 mol%), DMAP (2 equiv), epoxide (1 mL, 250 equiv), CO_2 (300 psig), CH_2Cl_2 (0.5 mL), 120 °C.[21]

[b] Yields were determined by comparing the ratio of product to substrate in the ^{1}H NMR of an aliquot of the reaction mixture. Known cyclic carbonate products were confirmed by MS and by comparing their NMR data with values reported in the literature. Data was available for 4-methyl-1,3-dioxolan-2-one,[29] 4-chloromethyl-1,3-dioxolan-2-one,[29] 4-phenyl-1,3-dioxolan-2-one,[29] 4-ethenyl-1,3-dioxolan-2-one,[30] and 4,4-dimethyl-1,3-dioxolan-2-one.[6] Analytical data for the remaining two products has not been reported and was confirmed by us.[31]

[c] CoTPP(Cl) (1 mol%).

[d] 100% *trans* product.

[e] CoTPP(Cl) (0.67 mol%), product *cis*:*trans* ratio (96:4).

ing[24] to produce the requisite metal alkoxide intermediate.[25] Thus, the presence of too much Lewis base could saturate the open metal binding site, thereby inhibiting the metal center's ability to activate and open the epoxide. We note that Darensbourg et al. have also proposed a similar initial mechanistic step for the coupling of CO_2 and cyclohexene oxide to form the corresponding polycarbonate using Cr^{III} salen/1-methylimidazole as the catalyst system.[26]

The mechanism shown in Scheme 1 can also be used to explain the diminishing of TOF at CO_2 pressures above 300 psig. High CO_2 concentration could eventually lead to the formation of a zwitterionic DMAP–CO_2 complex,[27] which would render this co-catalyst unavailable for the catalytic step where its coordination to the Lewis acidic metal center is necessary for the subsequent insertion of CO_2 into the metal alkoxide bond.[23]

Under the optimized reaction parameters, we found our Co^{III}(TPP)Cl/DMAP catalyst system to be active in the cycloaddition of CO_2 to a variety of terminal epoxides[28] (Table 2). Epoxides with aromatic, aliphatic, vinyl, electron-withdrawing, and electron-donating substituents all provided the cyclic carbonate products in near quantitative yield and 100% selectivity with only a slight change in reaction rate depending on the epoxide substituent. Significantly, our catalyst system is also active toward 1,1-disubstituted epoxides, as there are few reports on the efficient conversion of these substrates. Internal disubstituted epoxides were examined as well, and found to yield cyclic carbonates with a very high degree of stereospecificity. Both *cis*- and *trans*-2,3-epoxybutane were found to react with retention of configuration (Table 2, footnotes d and e), supporting our proposed mechanistic pathway where there is a double inversion of stereochemistry at the carbon center, that is attacked.

In conclusion, Co(TPP)Cl/DMAP is an excellent catalyst system for the coupling of CO_2 with a variety of epoxides to yield cyclic carbonates selectively and stereo-specifically. That ligated Co^{III} complexes are active for reaction 1 under moderate CO_2 pressure is quite exciting in view of the dearth of literature precedents for Co complexes in this reaction. We are actively investigating the mechanism, the catalyst scope with respect to other Co^{III} complexes, and the application of these Co^{III} catalysts in the synthesis of fine chemicals and polymers. These results will be reported in due course.

Acknowledgements

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References and notes

1. Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: New York, 1988.
2. Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155–174.
3. Biggadike, K.; Angell, R. M.; Burgess, C. M.; Farrell, R. M.; Hancock, A. P.; Harker, 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. J.; Walton, S.; Weston, H. E. *J. Med. Chem.* **2000**, *43*, 19–21.
4. Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951–976.
5. Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953–996.
6. Baba, A.; Nozaki, T.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1552–1554.
7. Bäckvall, J. E.; Karlsson, O.; Ljunggren, S. O. *Tetrahedron Lett.* **1980**, *21*, 4985–4988.
8. Calo, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. *Org. Lett.* **2002**, *4*, 2561–2563.
9. Fujinami, T.; Suzuki, T.; Kamiya, M.; Fukuzawa, S.; Sakai, S. *Chem. Lett.* **1985**, 199–200.
10. Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198–6202.
11. Kruper, W. J.; Dellar, D. D. *J. Org. Chem.* **1995**, *60*, 725–727.
12. Nomura, R.; Ninagawa, A.; Matsuda, H. *J. Org. Chem.* **1980**, *45*, 3735–3738.
13. Peppel, W. J. *Ind. Eng. Chem.* **1958**, *50*, 767–770.
14. Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526–4527.
15. Yang, H.; Gu, Y.; Deng, Y.; Shi, F. *Chem. Commun.* **2002**, 274–275.
16. Yano, T.; Matsui, H.; Koike, T.; Ishiguro, H.; Fujihara, H.; Yoshihara, M.; Maeshima, T. *Chem. Commun.* **1997**, 1129–1130.
17. Iwasaki, T.; Kihara, N.; Endo, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 713–719.
18. Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498–11499.
19. Shen et al. have reported that Co^{II} salen also catalyzed the formation of propylene carbonate in the presence of Lewis bases, see: Shen, Y.-M.; Duan, W.-L.; Shi, M. *J. Org. Chem.* **2003**, *68*, 1559–1562.
20. The Co^{III}TPP(Cl) complex was synthesized according to a known literature procedure, see: Tse et al. *Organometallics* **1998**, *17*, 2651–2655.
21. Representative procedure for the coupling reaction of epoxides and CO$_2$: On the bench top, a 125 mL stainless steel Parr high pressure reactor was charged with Co^{III}TPP(Cl)(20.0 mg, 2.76×10^{-5} mol), propylene oxide (5 mL, 4.15 g, 7.14×10^{-2} mol), DMAP (6.7 mg, 5.51×10^{-5} mol), and CH_2Cl_2 (1.0 mL). The reaction vessel was placed under a constant pressure of CO$_2$ for 5 min to allow the system to equilibrate and then heated to 120 °C for the allotted time. The vessel was then cooled to ambient temperature by placement in a dry ice/water bath. The pressure was then released and the contents transferred to a 50 mL round-bottom flask. Unreacted substrate and solvent were removed in vacuo and the product was then isolated via Kugelrohr distillation (65 °C/0.2 mmHg). Analysis of the product was carried out via GC–MS, GC (using an instrument equipped with FID detector and a 30 m HP-5 capillary column with 0.32 mm inner diameter and 0.25 mm film thickness. Temperature program: initial time = 0, initial temperature = 50 °C, rate = 15 °C/min; final time = 10 min, final temperature = 250 °C), and NMR.
22. No reaction was observed in the absence of Lewis base.
23. Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304–1309.
24. Increasing the Cl-concentration by the addition of excess NBu_4Cl does not lead to a significant increase in TOF, suggesting that the more Lewis basic DMAP is primarily responsible for the ring-opening of the Co-activated epoxide.
25. That the ring opening of the epoxide occurs at the least substituted position, as consistent with a nucleophilic ring-opening mechanism, should not change the stereochemistry at the more substituted carbon of the epoxide. This is indeed the case: the reaction of chirally pure (*S*)-(+)propylene oxide results in pure (*S*)-(+) propylene carbonate.
26. Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335–6342.
27. Although the DMAP–CO$_2$ adduct has not been characterized, the analogous DBU–CO$_2$ adduct has been isolated and characterized, see: Franco et al. *Tetrahedron Lett.* **2002**, *43*, 4091–4093.
28. Cyclohexene oxide was employed as substrate and found to yield only the corresponding polycarbonate.
29. Katzhend, J.; Sarel, S.; Ringel, I. *J. Chem. Soc., Perkin Trans. 2* **1972**, *14*, 2019–2025.
30. Lorincz, T.; Erden, I. *Synth. Commun.* **1986**, *16*, 123–130.
31. 4-Butyl-1,3-dioxolan-2-one: ^{1}H NMR (CD_2Cl_2): δ 0.92 (t, 3H, CH_3), 1.37 (m, 4H, CH_2), 1.69 (m, 1H, CH_2), 1.78 (m, 1H, CH_2), 4.05 (t, 1H, CH_2O), 4.50 (t, 1H, CH_2O), 4.70 (m, 1H, CHO). ^{13}C NMR (CD_2Cl_2): δ 14.12, 22.81, 27.00, 34.00, 70.02, 77.70, 155.55. HRCIMS: m/z Calcd for $C_7H_{13}O_3$ ([MH]$^+$): 145.0859. Found: 145.0858. 4-Benzyl-1,3-dioxolan-2-one: ^{1}H NMR (CD_2Cl_2): δ 2.97–3.13 (dd, 2H, benzylic protons, A and B of ABX system, $J_{AB} = 14.5$ Hz, $J_{AX} = J_{BX} = 7$ Hz), 4.15 (t, 1H, CH_2O), 4.44 (t, 1H, CH_2O), 4.92 (m, 1H, CHO), 7.23 (m, 2H, aromatic-*H*), 7.29 (m, 1H, aromatic-*H*), 7.34 (m, 2H, aromatic-*H*). ^{13}C NMR (CD_2Cl_2): δ 40.07, 69.16, 77.50, 127.93, 129.39, 129.90, 134.94, 155.22. HREIMS: m/z Calcd for $C_{10}H_{10}O_3$ ([M]$^+$): 178.0624. Found: 178.0623.