pubs.acs.org/IC

Highly Active Chromium Complexes Supported by Constrained Schiff-Base Ligands for Cycloaddition of Carbon Dioxide to Epoxides

Jiraya Kiriratnikom, Nattiya Laiwattanapaisarn, Kunnigar Vongnam, Nopparat Thavornsin, Pornpen Sae-ung, Sophon Kaeothip, Anucha Euapermkiati, Supawadee Namuangruk, and Khamphee Phomphrai*

Cite This: Inorg	. Chem. 2021, 60, 6147–6151	Read Online	
ACCESS	LIII Metrics & More	E Article Recommendations	Supporting Information

ABSTRACT: Novel constrained Schiff-base ligands (inden) were developed based on the well-known salen ligands. Chromium complexes supported by the constrained inden ligands were successfully synthesized and used as catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide (CO₂). The catalyst having *tert*-butyl (^tBu) groups as substituents in combination with tetrabutylammonium bromide (TBAB) as a cocatalyst exhibited very high catalytic activity with a turnover frequency of up to 14800 h⁻¹ for the conversion of CO₂ and propylene oxide into propylene carbonate exclusively at 100 °C and 300 psi of CO₂ under solvent-free conditions. The catalyst was found to be highly active for various epoxide substrates to produce terminal cyclic carbonates in 100% selectivity.

B ecause of public concerns of global warming as a result of increasing atmospheric carbon dioxide (CO_2) levels, CO_2 has been explored extensively as a promising feedstock for various important chemical productions such as urea, methanol, cyclic carbonates, and polycarbonates.¹⁻³ Among them, the cycloaddition reaction of CO_2 to epoxides, affording cyclic carbonates, is a commercially important reaction already exploited in numerous applications such as polar aprotic solvents for catalytic reactions,⁴ electrolytes for lithium-ion batteries used in electric vehicles and mobile devices,^{5,6} and precursors for valuable polymers and chemicals.⁶⁻⁸ The cycloaddition synthesis route of cyclic carbonates is a much greener alternative process compared to that using phosgene. However, CO_2 is highly stable and has low reactivity. Therefore, highly active catalysts are required for this simple but significant 100% atom economy transformation.

Several catalytic systems have been explored for CO₂/ epoxides cycloaddition reactions employing metal complexes such as Al, Cr, Co, Zn, and Fe ligated by a variety of wellknown supporting ligands such as porphyrin, salicylimine (salen), and Schiff-base ligands. $^{9-14}$ Among these ligands, dinitrogen dioxide-chelating salen ligands have been extensively studied as supporting ligands in catalysis because of simple ligand syntheses and tunable modifications for electronic and steric properties (Scheme 1).^{11,15-19} Among those active metal complexes, chromium complexes were found to be remarkable catalysts for the preparation of cyclic carbonates from CO_2 and a wide range of epoxides. They are highly stable and can be easily prepared from commercially available chromium(III) acetate or chloride as a starting material. The first chromium catalysts for cycloaddition were reported by Kruper and Dellar using a porphyrin ligand system.²⁰ Shortly after that, a large variety of chromium complexes based on salen ligands (Scheme 1a) were found to

Scheme 1. Chromium(III) Complexes Containing (a) Regular Salen and (b) Inden Ligands (this work)



efficiently catalyze the cycloaddition reaction of CO₂ to epoxides.^{11,21} In 2001, Paddock and Nguyen investigated binary (salen)Cr^{III} complexes/4-(dimethylamino)pyridine (DMAP) catalyst systems based on a cooperative mechanism requiring both (salen)CrIII complexes as a Lewis acid for epoxide activation and DMAP cocatalyst as a Lewis base for CO₂ activation.²² This binary system was very active for the propylene oxide $(PO)/CO_2$ cycloaddition reaction, obtaining a high turnover frequency (TOF) of 916 h^{-1} using [PO]:[Cr] = 1333:1 and 100 psi of CO₂ at 100 °C. In 2008, Sun et al. reported a bifunctional one-component catalyst system based on pyrrolidine (salen)Cr^{III}X complexes containing an electrophilic site (the metal center) and a nucleophilic unit (the strong organic base) in the same molecule.²³ This innovative intramolecular two-centered cooperative catalyst was highly active even at a high [PO]/[Cr] ratio of 5000:1 and 290 psi of

Received: December 21, 2020 Published: March 5, 2021



Communication





Figure 1. Synthetic procedure for (inden)Cr^{III} complexes.

 CO_2 at 80 °C, providing the highest TOF for chromium catalysts of 2120 h⁻¹. Motivated by the high potentials of cyclic carbonates in industry, we have set out to design a new highly active catalyst for the CO_2 /epoxides cycloaddition reactions based on the famous and successful salen ligand framework.

Conventional modifications of salen ligands have concentrated on variations of the aromatic substituents and diamine backbones such as R_{1-4} in Scheme 1a, giving ligands that can be systematically tuned for electron deficiency, steric hindrance, and chirality.^{11,15-18} While the development of salen-type ligands seems matured, we found that constraint modification around the aromatic ring and imine bond, as shown in Scheme 1b, has never been investigated. This novel ligand design has several promising advantages over the existing salen framework. For example, the coordinating N and O atoms on both sides are now restricted to being coplanar with respect to the phenyl rings, giving a more rigid coordination environment compared to salen ligands. The N-O distances could be lengthened due to constraint of the 5membered ring, resulting in a wider bite angle to the metal center and a larger active site available for substrate coordination. Therefore, the novel indanone-based ligands (inden) 1a-1c were synthesized via the condensation reaction of the corresponding substituted 7-hydroxy-1-indanone with ethylenediamine in moderate-to-high yield (see the Supporting Information, SI). Ligands 1b and 1c were characterized crystallographically (Figures S4 and S5). The average N-O distance (e.g., N1-O1) in ligand 1c is 2.663(4) Å, which is significantly longer (>0.1 Å) than the reported average N-O distance in the related nonconstrained salen ligand (2.555 Å).²⁴

The (inden)Cr^{III}Cl complexes 2a-2c were synthesized following a common preparation in high yield by reacting ligands 1a-1c with NaH, followed by CrCl₃·3THF in tetrahydrofuran (THF; Figure 1). Unfortunately, several attempts to crystallize the complexes for X-ray structural studies were unsuccessful. Therefore, computational studies of the related nonconstrained (salen)CrCl complex [compound A: Scheme 1a; $R_{1-2} = tert$ -butyl (^tBu) and $R_{3-4} = H$] in comparison with complex 2c were undertaken (Figure 2 and Table S2). The calculated charges on the Cr (+1.11 vs +1.10)and Cl (-0.42 vs -0.43) atoms are only slightly different in both compounds, suggesting that the electronic difference of the two compounds may not be significant. However, the ligand coordinations to Cr atoms are significantly different. The average N–O distance (e.g., N1–O1) in 2c is about 0.06 Å longer than that in compound A because of the more constrained 5-membered rings, giving a wider pocket at Cr atom. The average Cr–N bond distance in 2c is slightly longer (about 0.013 Å), while the average Cr-O and Cr-Cl bond distances are very similar to compound A. The shortest H-H



Figure 2. Structural comparison of compounds (a) A and (b) 2c with calculated bond distances (Å).

distance between the two ^tBu groups in 2c is about 0.036 Å longer than that in compound A (2.712 vs 2.748 Å), giving a wider pocket at Cr atom.

The catalytic activities of complexes 2a-2c for the PO/CO₂ cycloaddition reactions to cyclic propylene carbonate (PC) were then tested under the neat PO condition, as summarized in Table 1, entries 1-3, using a PO/cocatalyst/catalyst mole ratio of 5000:1:1 at 80 °C and 300 psi of CO2 for 1 h. Tetrabutylammonium bromide (TBAB) was used as a cocatalyst. Very low catalyst and cocatalyst loadings were used (0.02 mol %). All complexes were active for the cycloaddition reactions, giving conversions exclusively to PC at 18%, 19%, and 38% for complexes 2a-2c, respectively. Complex 2b having an ethylene backbone has a slightly higher TOF of 950 h^{-1} compared to complex 2a having a phenylene backbone. When 'Bu groups were incorporated into the ligand as in 2c, an exceptionally high TOF of 1900 h^{-1} was achieved. This unoptimized condition already gave a TOF comparable to the record-high TOF for chromium catalysts having intramolecularly linked electrophilic and nucleophilic centers [TOF = 2120 h⁻¹; $P(CO_2) = 290$ psi; 80 °C].²³ The reaction without the catalyst (entry 4) did not produce appreciable product, revealing that the presence of 2c is necessary. For comparison,

Table 1. Cycloaddition of CO_2 to PO by Chromium Catalysts^{*a*}



^aConditions: neat PO, 300 psi of CO₂, 80 °C, and 1 h. ^bCocatalysts. ^cDetermined by ¹H NMR of the crude reaction mixture. ^dMoles of PC produced per mole of chromium catalyst per hour. ^eReported conversion already subtracted background conversion from entry 9. ^fReaction temperature: 100 °C. Reported conversion in entry 12 already subtracted background conversion from entry 11.

the cycloaddition using A as a catalyst was carried out under the same conditions, giving a TOF of only 1250 h^{-1} (Table 1, entry 5). It is evident that 2c having constrained 5-membered rings is significantly more active, giving a TOF of over 50% higher than that using the related salen complex A.

To gain insight information on the cycloaddition reaction, computational calculations were performed and compared

pubs.acs.org/IC

between complexes A and 2c, as shown in Figure 3. The reaction starts with PO adsorption on the Cr atom (IC) having similar free energies for both compounds A and 2c. The Br⁻ ion then attacks PO as the ring-opening step, requiring free-energy barriers of 10.09 and 11.67 kcal/mol for A and 2c, respectively. The free-energy barrier for the subsequent CO_2 cycloaddition step is, however, much larger than the first step. The free-energy barrier for this step catalyzed by A (25.21 kcal/mol) is higher than that for 2c (22.96 kcal/mol), in line with the observed lower activity for A compared to 2c.

The cycloaddition reaction was further optimized using catalyst 2c in subsequent reactions. In addition to TBAB, other cocatalysts were investigated, as shown in Table S4 for tetrabutylammonium iodide, DMAP, bis(triphenylphosphine)iminium chloride, and 1,8-diazabicyclo[5.4.0]undec-7-ene under the same reaction conditions, giving TOFs ranging from 150 to 950 h⁻¹. However, these cocatalysts were still outperformed by TBAB. The equivalents of TBAB were then optimized by increasing them from 1 to 10. As anticipated, the TOF increased dramatically to 4300 h^{-1} (entry 6). Higher TOFs can be further achieved by increasing the amounts of PO (5000-20000 equiv) and TBAB (10-200 equiv) (entries 7-10). At this point, the amount of chromium catalyst is extremely low (0.005 mol %) but still gave the highest TOF at 11400 h⁻¹ for a PO/TBAB/2c ratio of 20000:200:1 (entry 10). Only a small background conversion (1%) from TBAB was observed at 80 °C (entry 9). When the temperature was increased from 80 to 100 °C (entry 12), the TOF increased dramatically to finally reach 14800 h^{-1} . When the reaction time was increased to 3 h, 100% conversion of PO was obtained with 94% isolated yield by flash chromatography.

The high efficiency of the 2c/TBAB binary system was further demonstrated for other terminal epoxides such as epichlorohydrin, hexene oxide, 3,4-epoxy-1-butene, styrene oxide, and 3-phenoxypropylene oxide, as shown in Table S5.



Figure 3. Free energy profiles for PO/CO₂ cycloaddition reactions using compounds A and 2c at 353.15 K.

All cycloaddition reactions gave very high TOF (2750-16600 h^{-1}) with 100% selectivity to cyclic carbonates. The highest TOF of 16600 h^{-1} belongs to the cycloaddition with epichlorohydrin. The cycloaddition with internal epoxides such as pentene oxide and cyclohexene oxide exhibited only low-to-moderate activity (TOF of 390 and 168 h⁻¹, respectively) possibly because of the steric hindrance during the nucleophilic ring-opening of the epoxide.^{23,25} However, the CO₂ cycloaddition to cyclohexene oxide gave both cyclic carbonate and atactic polycarbonate (without ether linkage) in the ratio of 64:36. The gel permeation chromatography trace of poly(cyclohexene carbonate) exhibited bimodal distributions with $M_{\rm p}$ of 11900 Da ($\bar{D} = 1.02$) and 5800 Da ($\bar{D} = 1.04$) (see Figure S23). The presence of bimodal distributions was commonly found for the copolymerization of cyclohexene oxide with CO₂ typically attributed to the trace of 1,2-cyclohexanediol impurities.²⁶ Comparisons of the activities of our catalyst with other reported chromium catalyst systems for these epoxides are rather difficult because very different reaction conditions were applied in the literature [for example, T = 25-130 °C and $P(CO_2) = 1-780$ atm].^{20,22,25,27-2} However, the previously reported TOFs (h^{-1}) in general are on the order of hundreds rather than thousands, as shown in this work.

In summary, the novel constrained (inden)Cr^{III} complexes were successfully developed and found to be highly active in the cycloaddition reactions of CO_2 to epoxides in the presence of TBAB as a cocatalyst. The Cr^{III}/TBAB catalysts are highly active even at low catalyst loading of 0.005 mol %, giving PC exclusively with a very high TOF of 14800 h^{-1} . The binary catalyst system can be extended to other terminal and internal epoxides with high catalytic activities. The ease of ligand synthesis and modification of the catalyst's structure is the major advantage of this type of ligand that will allow a systematic tailoring of the catalytic activities and selectivity. The reported novel constrained inden ligand framework was proven to be the major successful development over the existing well-known salen ligands. The constrained inden metal complexes could also be applied in place of several other salenbased metal complexes already exploited in a wide range of catalytic processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03732.

Complete details for the crystallographic study of ligands 1b-1c, details for the experimental synthesis, cycloaddition reactions, characterization of 1a-1c, 2a-2c, and the corresponding cyclic carbonates and polycarbonate from CO₂/epoxide cycloaddition, and computational studies (PDF)

Accession Codes

CCDC 2050712 and 2050713 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Khamphee Phomphrai – Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Wang Chan, Rayong 21210, Thailand; orcid.org/0000-0002-3132-680X; Email: khamphee.p@vistec.ac.th

Authors

- Jiraya Kiriratnikom Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Wang Chan, Rayong 21210, Thailand
- Nattiya Laiwattanapaisarn Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Wang Chan, Rayong 21210, Thailand
- Kunnigar Vongnam Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Wang Chan, Rayong 21210, Thailand
- Nopparat Thavornsin Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Wang Chan, Rayong 21210, Thailand
- **Pornpen Sae-ung** Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Wang Chan, Rayong 21210, Thailand
- Sophon Kaeothip Corporate Innovation, Science and Innovation, PTT Global Chemical Public Company Ltd., Chatuchak, Bangkok 10900, Thailand
- Anucha Euapermkiati Corporate Innovation, Science and Innovation, PTT Global Chemical Public Company Ltd., Chatuchak, Bangkok 10900, Thailand
- Supawadee Namuangruk National Nanotechnology Center, National Science and Technology Development Agency, Klong Luang 12120, Pathum Thani, Thailand

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c03732

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge financial support from the PTT Global Chemical Public Company Ltd. Instrumental support from Frontier Research Center, VISTEC, is gratefully acknowledged. This work was partially supported by the NANOTEC, NSTDA, Ministry of Science and Technology, through its program of Research Network NANOTEC.

REFERENCES

(1) Chauvy, R.; Meunier, N.; Thomas, D.; De Weireld, G. Selecting Emerging CO_2 Utilization Products for Short- to Mid-Term Deployment. *Appl. Energy* **2019**, 236, 662–680.

(2) Otto, A.; Grube, T.; Schiebahn, S.; Stolten, D. Closing the Loop: Captured CO_2 as a Feedstock in the Chemical Industry. *Energy Environ. Sci.* **2015**, *8*, 3283–3297.

(3) Sun, Y.; Lin, Z.; Peng, S. H.; Sage, V.; Sun, Z. A Critical Perspective on CO₂ Conversions into Chemicals and Fuels. *J. Nanosci. Nanotechnol.* **2019**, *19*, 3097–3109.

(4) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. Organic Carbonates as Solvents in Synthesis and Catalysis. *Chem. Rev.* **2010**, *110*, 4554–4581.

(5) Nie, M.; Chalasani, D.; Abraham, D. P.; Chen, Y.; Bose, A.; Lucht, B. L. Lithium Ion Battery Graphite Solid Electrolyte Interphase Revealed by Microscopy and Spectroscopy. *J. Phys. Chem. C* 2013, *117*, 1257–1267.

(6) Kamphuis, A. J.; Picchioni, F.; Pescarmona, P. P. CO₂-Fixation into Cyclic and Polymeric Carbonates: Principles and Applications. *Green Chem.* **2019**, *21*, 406–448.

(7) Maeda, C.; Miyazaki, Y.; Ema, T. Recent Progress in Catalytic Conversions of Carbon Dioxide. *Catal. Sci. Technol.* **2014**, *4*, 1482.

(8) Taherimehr, M.; Pescarmona, P. P. Green Polycarbonates Prepared by the Copolymerization of CO_2 with Epoxides. *J. Appl. Polym. Sci.* **2014**, 131, 41141.

(9) North, M.; Pasquale, R.; Young, C. Synthesis of Cyclic Carbonates from Epoxides and CO₂. *Green Chem.* **2010**, *12*, 1514.

(10) Buttner, H.; Longwitz, L.; Steinbauer, J.; Wulf, C.; Werner, T. Recent Developments in the Synthesis of Cyclic Carbonates from Epoxides and CO₂. *Top. Curr. Chem.* **2017**, *375*, 50.

(11) Decortes, A.; Castilla, A. M.; Kleij, A. W. Salen-Complex-Mediated Formation of Cyclic Carbonates by Cycloaddition of CO₂ to Epoxides. *Angew. Chem., Int. Ed.* **2010**, *49*, 9822–9837.

(12) Shaikh, R. R.; Pornpraprom, S.; D'Elia, V. Catalytic Strategies for the Cycloaddition of Pure, Diluted, and Waste CO_2 to Epoxides under Ambient Conditions. *ACS Catal.* **2018**, *8*, 419–450.

(13) Martín, C.; Fiorani, G.; Kleij, A. W. Recent Advances in the Catalytic Preparation of Cyclic Organic Carbonates. *ACS Catal.* **2015**, *5*, 1353–1370.

(14) Qin, Y.; Guo, H.; Sheng, X.; Wang, X.; Wang, F. An Aluminum Porphyrin Complex with High Activity and Selectivity for Cyclic Carbonate Synthesis. *Green Chem.* **2015**, *17*, 2853–2858.

(15) Cozzi, P. G. Metal-Salen Schiff Base Complexes in Catalysis: Practical Aspects. *Chem. Soc. Rev.* 2004, 33, 410-421.

(16) Shaw, S.; White, J. D. Asymmetric Catalysis Using Chiral Salen-Metal Complexes: Recent Advances. *Chem. Rev.* **2019**, *119*, 9381– 9426.

(17) Matsumoto, K.; Saito, B.; Katsuki, T. Asymmetric Catalysis of Metal Complexes with Non-Planar ONNO Ligands: Salen, Salalen and Salan. *Chem. Commun.* **2007**, 3619–3627.

(18) Baleizão, C.; Garcia, H. Chiral Salen Complexes: An Overview to Recoverable and Reusable Homogeneous and Heterogeneous Catalysts. *Chem. Rev.* **2006**, *106*, 3987–4043.

(19) Coates, G. W.; Moore, D. R. Discrete Metal-Based Catalysts for the Copolymerization of CO_2 and Epoxides: Discovery, Reactivity, Optimization, and Mechanism. *Angew. Chem., Int. Ed.* **2004**, 43, 6618–6639.

(20) Kruper, W. J.; Dellar, D. D. Catalytic Formation of Cyclic Carbonates from Epoxides and CO_2 with Chromium Metalloporphyrinates. J. Org. Chem. **1995**, 60, 725–727.

(21) Darensbourg, D. J. Making Plastics from Carbon Dioxide: Salen Metal Complexes as Catalysts for the Production of Polycarbonates from Epoxides and CO₂. *Chem. Rev.* **2007**, *107*, 2388–2410.

(22) Paddock, R. L.; Nguyen, S. T. Chemical CO_2 Fixation: Cr(III) Salen Complexes as Highly Efficient Catalysts for the Coupling of CO_2 and Epoxides. J. Am. Chem. Soc. **2001**, 123, 11498–11499.

(23) Zhang, X.; Jia, Y.-B.; Lu, X.-B.; Li, B.; Wang, H.; Sun, L.-C. Intramolecularly Two-Centered Cooperation Catalysis for the Synthesis of Cyclic Carbonates from CO_2 and Epoxides. *Tetrahedron Lett.* **2008**, *49*, 6589–6592.

(24) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. Cyclohexene $Oxide/CO_2$ Copolymerization Catalyzed by Chromium(III) Salen Complexes and N-Methylimidazole: Effects of Varying Salen Ligand Substituents and Relative Cocatalyst Loading. *Inorg. Chem.* **2004**, *43*, 6024–6034. (25) Cuesta-Aluja, L.; Djoufak, M.; Aghmiz, A.; Rivas, R.; Christ, L.; Masdeu-Bultó, A. M. Novel Chromium (III) Complexes with N4-Donor Ligands as Catalysts for the Coupling of CO₂ and Epoxides in Supercritical CO₂. J. Mol. Catal. A: Chem. **2014**, 381, 161–170.

(26) Della Monica, F.; Maity, B.; Pehl, T.; Buonerba, A.; De Nisi, A.; Monari, M.; Grassi, A.; Rieger, B.; Cavallo, L.; Capacchione, C. [OSSO]-Type Iron(III) Complexes for the Low-Pressure Reaction of Carbon Dioxide with Epoxides: Catalytic Activity, Reaction Kinetics, and Computational Study. ACS Catal. **2018**, *8*, 6882–6893.

(27) Castro-Osma, J. A.; Lamb, K. J.; North, M. Cr(salophen) Complex Catalyzed Cyclic Carbonate Synthesis at Ambient Temperature And Pressure. ACS Catal. 2016, 6, 5012-5025.

(28) Adolph, M.; Zevaco, T. A.; Altesleben, C.; Walter, O.; Dinjus, E. New Cobalt, Iron and Chromium Catalysts Based on Easy-to-Handle N4-Chelating Ligands for the Coupling Reaction of Epoxides with CO₂. *Dalton Trans.* **2014**, *43*, 3285–3296.

(29) Dean, R. K.; Devaine-Pressing, K.; Dawe, L. N.; Kozak, C. M. Reaction of CO_2 with Propylene Oxide and Styrene Oxide Catalyzed by a Chromium(III) Amine-Bis(phenolate) Complex. *Dalton Trans.* **2013**, *42*, 9233–9244.