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Formation of Cyclic Carbonates from Carbon Dioxide and Epoxides Coupling Reactions Efficiently Catalyzed by Robust, Recyclable One-Component Aluminum-Salen Complexes

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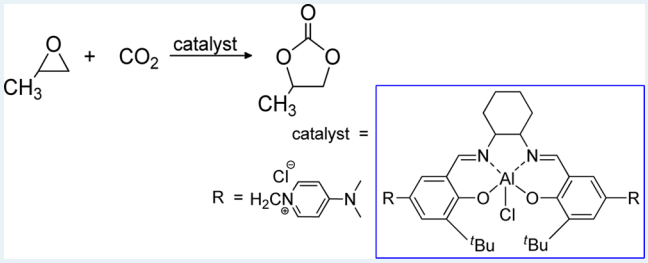
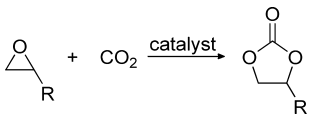
ABSTRACT: Aluminum salen complexes bearing appended quaternary ammonium salt substituents have been synthesized and shown to be effective catalysts for the coupling of epoxides and carbon dioxide to generate cyclic carbonates. ^{27}Al NMR spectra have demonstrated that these exist as both five- and six-coordinate Al(III) species in dimethylsulfoxide (DMSO) solution, whereas only a five-coordinate Al(III) species was detected in the (salen)AlCl analogue in the presence of an external onium salt. The onium salt group tethered on the salen ligand was found to play an important role in enhancing the catalytic activity. The effects of reaction variables such as temperature, time, pressure, molar ratio of epoxide to catalyst on the catalytic performance were systematically investigated. These bifunctional catalysts were found to be highly stable to moisture and oxygen, resistant to impurities, and recyclable with only minor losses in catalytic activity.



KEYWORDS: *carbon dioxide fixation, catalyst design, catalyst recycling, Schiff bases, aluminum*

INTRODUCTION

Carbon capture and storage technologies have experienced significant advancements over the past decade. For example, the use of metal−organic frameworks (MOFs) provides a novel solid-state method for CO_2 adsorption and separation which has undergone tremendous progress over recent years.[1] This represents potential replacement technology for the long practiced aqueous alkanolamine absorbents currently used for CO_2 scrubbing.[2] Hence, it can be anticipated that these innovations will lead to effective means for controlling CO_2 emissions at coal- and natural gas-based power plants and numerous other CO_2-emitting industrial facilities. Some of this large surplus of sequestered anthropogenic CO_2 provides opportunities for its utilization as an inexpensive source of chemical carbon, such as the use of CO_2 as a feedstock for chemical synthesis. One such class of chemicals which are widely used directly or as synthetic intermediates are cyclic organic carbonates produced from the coupling of CO_2 and epoxides (eq 1).[3]



(1)

Because cyclic carbonates are utilized in such large-scale processes, such as aprotic high-boiling polar solvents and electrolytes for lithium-ion batteries, numerous catalyst systems have been developed to promote this transformation.[4−11] Prominent among these are a variety of metal salen complexes because of their ease of synthesis, while varying the steric and electronic properties about the metal centers. In general, these catalysts require the addition of an onium salt cocatalyst to achieve effective activity. Recently, several (salen)CoX derivatives have been prepared which contain the quaternary onium salt tethered to the salen ligand, thereby affording a single component catalyst (Figure 1).[12−18] In this instance, the role of the tethered ammonium salt is to hinder cyclic carbonate formation by electrostatically attracting the anionic growing polymer chain, thereby inhibiting it from rapidly

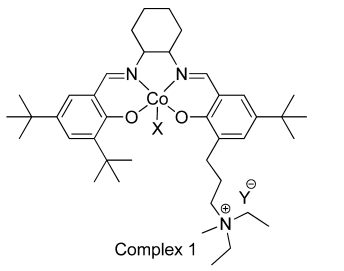


Figure 1. Lu's asymmetric bifunctional (salen)CoX complexes.[18].

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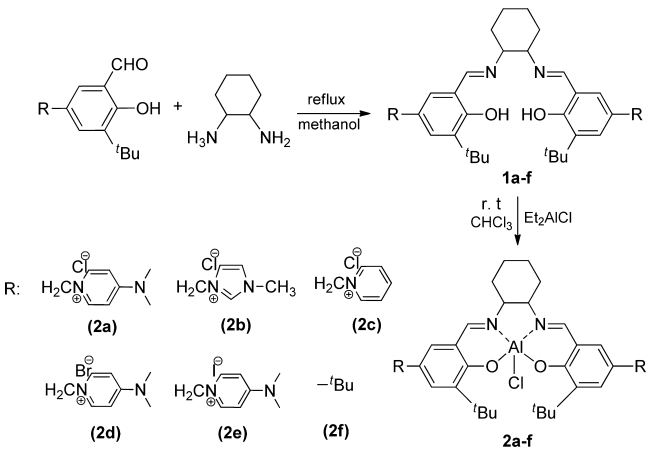
backbiting upon itself when it becomes detached from the metal center during the epoxide ring-opening process. Hence, the selectivity for copolymer vs cyclic carbonate is greatly enhanced in this case as compared to the analogues binary catalytic systems where the onium salt is not attached to the metal salen complex.

In efforts to use more environmentally benign metal complexes for the CO_2/epoxide coupling reaction, aluminum is a good choice. Indeed, there is much precedent in the literature for the employment of (salen)aluminum or (porphyrin)aluminum complexes in the presence of quaternary ammonium or phosphonium salts serving as binary catalysts for transforming CO_2/epoxides to either polycarbonates or cyclic carbonates.[7−9,19−26] In 2009, North and co-workers described one-component bimetallic μ-oxoaluminum(salen) complexes bearing quaternary ammonium groups for the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide.[27] Furthermore, this catalyst system was supported on silica and recycled in batch reactions with a modest loss in catalytic activity. For example, over four consecutive catalytic cycles for styrene oxide/CO_2 to styrene carbonate catalytic activity decreased by 60%. More recently, these researchers have successfully integrated this catalyst system for the production of cyclic carbonates from CO_2 produced by the combustion of methane.[28,29] In addition, a large variety of heterogeneous catalyst systems have been reported for the effective separation of metal-salen complexes from the product of epoxide/CO_2 coupling reactions.[30]

In this Article, we wish to report on the synthesis of a series of (salen)AlCl derivatives which contain quaternary ammonium salts tethered to the salen ligand (Scheme 1). The catalytic activity of these derivatives for the coupling of epoxides and carbon dioxide to provide cyclic carbonates in the absence of organic solvents is evaluated and compared to their binary catalyst analogues. Catalyst recycling studies were carried out which show that there is very minor loss in catalytic activity following several batch catalytic runs.

Scheme 1



EXPERIMENTAL SECTION

Reagents and Methods. All manipulations of air and/or moisture-sensitive compounds were carried out using standard Schenk techniques under a pure nitrogen atmosphere. 3, 5-di-*tert*-butyl salicylaldehyde and diethylaluminum chloride (Et_2AlCl) were purchased from Aldrich and used as received. 5-Chloromethyl-3-*tert*-butylsalicylaldehyde was synthesized according to the published procedure.[31] 5-Bromomethyl-3-*tert*-butyl-2-hydroxybenzaldehyde was prepared similar to the process described in the reference replacing concentrated hydrochloric acid with concentrated hydrobromic acid.[31] (1R, 2R)-1, 2-cyclohexanediamine was resolved from a technical grade cis−trans mixture according to the literature.[32] Propylene oxide (PO) was purchased from Sinopharm Chemical Reagent Co. Ltd. and distilled over calcium hydride under a nitrogen atmosphere. Carbon dioxide (99.99% purity) was used without further purification. Toluene was refluxed and distilled from Na-benzophenone under dry nitrogen. 4-(Dimethylamino) pyridine, *N*-methyl imidazole, pyridine, and benzyl chloride were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

^{1}H NMR spectra of ligands were recorded on a Bruker AV 400 M in $CDCl_3$, whereas the spectra of complexes **2a−f** were obtained in DMSO-d_6. ^{13}C NMR spectra of complexes **2a−f** were measured on a Bruker AV 400 M (100.6 MHz) spectrometer using DMSO-d_6 as solvent. ^{27}Al NMR spectra were recorded on a Bruker AV 400 M (104.3 MHz) spectrometer in DMSO-d_6. All chemical shifts are provided in parts per million using tetramethylsilane as an internal reference at ambient temperature. IR spectra of complexes **2a−f** were measured on a Bruker Vector 22 spectrometer using Nujol mull at 4 cm^{-1} resolution. UV−visible spectroscopy was performed in CH_3OH on a UV-CARY300 spectrometer.

Synthesis of Salicylaldehydes Derivatives a−e. The salicylaldehyde derivatives were synthesized as reported in the literature, and their ^{1}H NMR spectra are listed below.[14]

(**a**) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.92 (s, 1H, OH), 9.93 (s, 1H, CHO), 8.82 (s, 2H, CH of DMAP), 7.95 (s, 1H, Ph-H), 7.60 (s, 1H, Ph-H), 6.95 (s, 2H, CH of DMAP), 5.73 (s, 2H, Ph−CH_2), 3.23 (s, 6H, N−CH_3), 1.39 (s, 9H, *tert*-Bu) ppm.

(**b**) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.92 (s, 1H, OH), 10.76 (s, 1H, N=CH-N), 9.94(s, 1H, CHO), 7.87 (s, 2H, N−CH=CH-N), 7.58(s, 2H, N−CH=CH-N), 7.2 4 (s, 2H, Ph-H), 7.16 (s, 2H, Ph-H), 5.38 (s, 2H, Ph−CH_2), 3.91 (s, 3H, N−CH_3), and 1.39 (s, 9H, *tert*-Bu) ppm.

(**c**) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.97 (s, 1H, OH), 9.93 (s, 1H, CHO), 9.81 (s, 2H, CH of pyridine), 8.40 (s, 1H, CH of pyridine), 8.14 (s, 1H, Ph-H), 8.03 (s, 2H, CH of pyridine), 7.61 (s, 1H, Ph-H), 6.64 (s, 2H, Ph−CH_2), and 1.38 ppm (s, 9H, *tert*-Bu) ppm.

(**d**) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.92 (s, 1H, OH), 9.94 (s, 1H, CHO),8.76 (s, 2H, CH of DMAP), 7.9 5(s, 1H, Ph-H), 7.61(s, 1H, Ph-H), 6.89 (s, 2H, CH of DMAP), 5.7 1(s, 2H, Ph−CH_2), 3.23 (s, 6H, N−CH_3), 1.39 (s, 9H, *tert*-Bu) ppm.

(**e**) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.92 (s, 1H, OH), 9.97 (s, 1H, CHO),8.64 (s, 2H, CH of DMAP), 7.95 (s, 1H, Ph-H), 7.61(s, 1H, Ph-H), 6.90 (s, 2H, CH of DMAP), 5.66 (s, 2H, Ph−CH_2), 3.23 (s, 6H, N−CH_3), 1.39 (s, 9H, *tert*-Bu) ppm.

General Procedure for the Preparation of Salen Ligands 1a−f. The Schiff base ligands were prepared by heating under reflux an ethanolic solution of (*1R, 2R*)-1, 2-cyclohexanediamine and the corresponding salicylaldehydes derivatives (6 mmol) in a 1:2 molar ratio at reflux. Following, the solvent was evaporated to dryness, and the residue was dissolved in CH_2Cl_2/ethyl acetate (4:3 v/v). The resulting solution was allowed to evaporate slowly at ambient temper-

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ature during which time the ligands precipitated out of solution, were isolated by filtration, and washed with ethyl acetate and diethyl ether. The ^{1}H and ^{13}C NMR spectra are listed below.

(**1a**) IR 1648 ($\nu_{C=N}$), 1565 (Ph ving $\nu_{C=C}$), and 1272 cm^{-1} (ν_{Ar-O}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.23 (*s*, 2H, OH), 8.60 (*s*, 4H, CH of DMAP), 8.28 (*s*, 2H, N=C), 7.27 (*s*, 2H, Ph-H), 7.18 (*s*, 2H, Ph-H), 6.91 (*s*, 4H, CH of DMAP), 5.32-5.58 (*s*, 4H, Ph−CH_2), 3.34−3.47 (*m*, 2H, CH), 3.20 (*s*, 12H, N−CH_3), 1.47−2.06 (*m*, 8H, $(CH_2)_2$), and 1.34 (*s*, 18H, *tert*-Bu) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 165.1, 161.5, 156.2, 142.2, 138.6, 130.6, 129.9, 123.0, 118.8, 71.4, 60.6, 40.4, 34.9, 29.3, and 24.1 ppm. UV−vis: 330, 291, and 220 nm. Anal. Calcd for $C_{44}H_{60}Cl_2N_6O_2$ C, 68.11; H, 7.79; N, 10.83; Found: C, 67.83; H, 7.67; N, 10.65.

(**1b**) IR 1647 ($\nu_{C=N}$), 1560 (Ph ving $\nu_{C=C}$), and 1274 cm^{-1} (ν_{Ar-O}). ^{1}H NMR(400 MHz, $CDCl_3$): δ = 14.24 (*s*, 2H, OH), 10.65 (*s*, 2H, N=CH-N), 8.25 (*s*, 2H, CH=N), 7.58 (*s*, 2H, N−CH=CH-N), 7.32 (*s*, 2H, *N*-CH=CH-N), 7.13 (*s*, 2H, Ph-H), 6.96 (*s*, 2H, Ph-H), 5.32−5.47 (*s*, 4H, Ph−CH_2), 4.03 (*s*, 6H, N−CH_3), 3.33−3.46 (*m*, 2H, CH), 1.48−2.06 (*m*, 8H, $(CH_2)_2$), and 1.36 (*s*, 18H, *tert*-Bu) ppm. UV−vis: 324, 257, and 223 nm. Anal. Calcd for $C_{38}H_{52}Cl_2N_6O_2$ C, 65.60; H, 7.53; N, 12.08; Found: C, 65.64; H, 7.58; N, 12.03.

(**1c**) [14] IR 1631 ($\nu_{C=N}$), 1598 (Ph ving $\nu_{C=C}$), and 1272 cm^{-1} (ν_{Ar-O}).^{1}H NMR($CDCl_3$): (δ H, ppm): 14.28(s, 2H, OH), 9.92(s, 4H, CH of pyridine), 8.36(s, 2H, C=N), 8.21(s, 2H, CH of pyridine), 8.01(s, 4H, CH of pyridine), 7.47(s, 2H, Ph-H), 7.20(s, 2H, Ph-H), 6.27 (*s*, 4H, Ph−CH_2), 3.47(m, 2H, CH-N), 1.45−2.13(m, 8H, $(CH_2)_2$), and 1.35(s, 18H, *tert*-Bu) ppm. UV−vis: 333, 263, and 222 nm. Anal. Calcd for $C_{40}H_{60}N_4O_2$ C, 69.65; H, 7.31; N, 8.12; Found: C, 69.73; H, 7.29; N, 8.40.

(**1d**) IR 1648 ($\nu_{C=N}$), 1569 (Ph ving $\nu_{C=C}$), and 1272 cm^{-1} (ν_{Ar-O}). ^{1}H NMR (400 MHz, $CDCl_3$): δ =14.23 (s, 2H, OH), 8.56 (s, 4H, CH of DMAP), 8.30 (s, 2H, N=C), 7.28 (s, 2H, Ph-H), 7.22 (s, 2H, Ph-H), 6.90 (s, 4H, CH of DMAP), 5.33−5.59 (s, 4H, Ph−CH_2), 3.37 (m, 2H, CH), 3.14 (s, 12H, N−CH_3), 1.49−2.02 (m, 8H, $(CH_2)_2$), and 1.34 (s, 18H, *tert*-Bu) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 165.1, 161.5, 156.2, 142.2, 138.7, 130.6, 130.6, 122.8, 118.5, 108.2, 71.5, 60.6, 40.5, 34.9, 29.3, and 24.1 ppm. UV−vis: 331, 292, and 220 nm. Anal. Calcd for $C_{44}H_{60}Br_2N_6O_2$ C, 61.11; H, 6.99; N, 9.72; Found: C, 61.13; H, 6.98; N, 9.80.

(**1e**) IR 1649 ($\nu_{C=N}$), 1567 (Ph ving $\nu_{C=C}$), and 1272 cm^{-1} (ν_{Ar-O}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.22 (*s*, 2H, OH), 8.46 (*s*, 4H, CH of DMAP), 8.35 (*s*, 2H, N=C), 7.29 (*s*, 2H, Ph-H), 7.26 (*s*, 2H, Ph-H), 6.89 (*s*, 4H, CH of DMAP), 5.30−5.54 (*s*, 4H, Ph−CH_2), 3.35−3.48 (*m*, 2H, CH), 3.22 (*s*, 12H, N−CH_3), 1.48−2.04 (*m*, 8H, $(CH_2)_2$), and 1.35 (*s*, 18H, *tert*-Bu) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 164.9, 161.6, 156.2, 142.1, 138.8, 130.5, 129.9, 122.5, 118.5, 108.3, 71.3, 60.6, 40.8, 35.0, 29.4, and 24.1 ppm.UV−vis: 330, 292, and 219 nm. Anal. Calcd for $C_{44}H_{60}I_2N_6O_2$ C, 55.12; H, 6.31; N, 8.77; Found: C, 55.13; H, 6.38; N, 8.77.

General Synthesis of Aluminum Complexes 2a−f. The aluminum salen derivatives were synthesized according to the literature method with only slight modification.[33] Et_2AlCl (1.0 M solution in toluene, 1.01 mL) was added to a solution of 1.0 mmol (*R, R*-salen)H_2 in 20 mL of dichloromethane, and the mixture stirred under reflux for 2 h. The complexes were obtained as yellow powders following the removal of volatiles under vacuum.

Complex ***2a***. IR 1647 ($\nu_{C=N}$), 1558 (Ph ving $\nu_{C=C}$), 1255 cm^{-1} (ν_{Ar-O}). ^{1}H NMR(400 MHz, DMSO-d_6): δ = 8.55 (*s*, 4H, CH of DMAP), 8.30 (*s*, 2H, CH=N), 7.54 (*s*, 2H, Ph-H), 7.50 (*s*, 2H, Ph-H), 7.09 (*s*, 4H, CH of DMAP), 5.36 (*s*, 4H, Ph−CH_2), 3.36 (*m*, 2H, CH), 3.16 (*s*, 12H, N−CH_3), 1.95 (*m*, 4H, $(CH_2)_2$), 1.43 (*s*, 18H, *tert*-Bu), and 0.85−1.03 (*m*, 4H, $(CH_2)_2$) ppm. ^{13}C NMR (100.4 MHz, DMSO-d_6): δ = 163.7, 155.8, 141.9, 140.5, 133.1, 131.7, 128.1, 122.1, 119.6, 107.9, 63.3, 59.2, 54.9, 48.5, 35.1, 29.5, 26.8, 23.3, and 21.0 ppm. ^{27}Al NMR (104.3 MHz, DMSO-d_6): δ = 72.65 and 6.60 ppm. UV−vis: 351, 280, and 236 nm. Anal. Calcd for $C_{44}H_{58}AlCl_3N_6O_2$ C, 63.19; H, 6.99; N, 10.05; Found: C, 62.83; H, 6.67; N, 10.25.

Complex ***2b***. IR 1634 ($\nu_{C=N}$), 1554 (Ph ving $\nu_{C=C}$), and 1249 cm^{-1} (ν_{Ar-O}). ^{1}H NMR(400 MHz, DMSO-d_6): δ = 9.60 (*s*, 2H, *N* = CH-N), 8.34 (*s*, 2H, CH=N), 7.90(*s*, 2H, N−CH=CH-N), 7.79 (*s*, 2H, N−CH=CH-N), 7.59 (*s*, 2H, Ph-H), 7.50 (*s*, 2H, Ph-H), 5.37 (*s*, 4H, Ph−CH_2), 3.91 (*s*, 6H, N−CH_3), 3.33−3.44 (*m*, 2H, CH), 1.54−1.94 (*m*, 4H, $(CH_2)_2$), 1.51(s, 18H, *tert*-Bu), and 0.82−1.07 (*m*, 4H, $(CH_2)_2$) ppm. ^{13}C NMR (100.4 MHz, DMSO-d_6): δ = 163.6, 140.4, 137.3, 136.6, 133.4, 128.7, 128.2, 125.3, 122.2, 121.2, 119.6, 63.3, 55.9, 51.8, 35.1, 29.5, 26.8, 23.3, 21.0, and 18.5 ppm. ^{27}Al NMR (104.3 MHz, DMSO-d_6): δ = 71.50 and 12.26 ppm. UV−vis: 349, 280, and 240 nm. Anal. Calcd for $C_{38}H_{50}AlCl_3N_6O_2$ C, 60.36; H, 6.66; N, 11.11; Found: C, 60.64; H, 6.58; N, 11.03.

Complex ***2c***. IR 1633 ($\nu_{C=N}$), 1545 (Ph ving $\nu_{C=C}$), and 1250 cm^{-1} (ν_{Ar-O}). ^{1}H NMR(400 MHz, DMSO-d_6): δ = 9.35(*m*, 4H, py-H), 8.65(*m*, 2H, py-H), 8.29 (*s*, 2H, CH=N), 8.22(*m*, 4H, py-H), 7.65 (*s*, 4H, Ph-H), 5.83 (*s*, 4H, Ph−CH_2), 3.45 (*m*, 2H, CH), 1.50−1.93 (*m*, 8H, $(CH_2)_2$), and 1.44 (*s*, 18H, *tert*-Bu) ppm. ^{13}C NMR (100.4 MHz, DMSO-d_6): δ = 164.1, 145.7, 144.6, 134.1, 128.3, 120.7, 119.7, 55.9, 54.9, 35.1, 29.5, and 18.5 ppm. ^{27}Al NMR (104.3 MHz, DMSO-d_6): δ = 69.87 and 6.38 ppm. UV−vis: 356, 280, and 235 nm. Anal. Calcd for $C_{40}H_{48}AlCl_3N_4O_2$ C, 64.04; H, 6.45; N, 7.47; Found: C, 64.18; H, 6.52; N, 7.53.

Complex ***2d***. IR 1648 ($\nu_{C=N}$), 1558 (Ph ving $\nu_{C=C}$), 1257 cm^{-1} (ν_{Ar-O}). ^{1}H NMR(400 MHz, DMSO-d_6): δ = 8.59 (*s*, 4H, CH of DMAP), 8.36 (*s*, 2H, CH=N), 7.60 (*s*, 2H, Ph-H), 7.56 (*s*, 2H, Ph-H), 7.15 (*s*, 4H, CH of DMAP), 5.41 (*s*, 4H, Ph−CH_2), 3.44 (*m*, 2H, CH), 3.21 (*s*, 12H, N−CH_3), 1.51−1.99 (*m*, 4H, $(CH_2)_2$), 1.49 (*s*, 18H, *tert*-Bu), and 0.87−1.12 (*m*, 4H, $(CH_2)_2$) ppm. ^{13}C NMR (100.4 MHz, DMSO-d_6): δ = 163.7, 155.8, 141.9, 140.5, 133.1, 131.7, 122.0, 119.6, 107.9, 63.3, 59.2, 54.9, 48.5, 35.1, 29.5, and 18.5 ppm. ^{27}Al NMR (104.3 MHz, DMSO-d_6): δ = 70.66 and 4.14 ppm. UV−vis: 355, 284, and 236 nm. Anal. Calcd for $C_{44}H_{58}AlBr_2ClN_6O_2$ C, 57.12; H, 6.32; N, 9.08; Found: C, 57.18; H, 6.24; N, 9.15.

Complex ***2e***. IR 1647 ($\nu_{C=N}$), 1556 (Ph ving $\nu_{C=C}$), 1255 cm^{-1} (ν_{Ar-O}). ^{1}H NMR(400 MHz, DMSO-d_6): δ = 8.53 (*s*, 4H, CH of DMAP), 8.32 (*s*, 2H, CH=N), 7.54 (*s*, 2H, Ph-H), 7.12 (*s*, 4H, CH of DMAP), 5.30 (*s*, 4H, Ph−CH_2), 3.44 (*m*, 2H, CH), 3.21 (*s*, 12H, N−CH_3), 1.54−1.96 (*m*, 4H, $(CH_2)_2$), 1.51(*s*, 18H, *tert*-Bu), and 0.87−1.06 (*m*, 4H, $(CH_2)_2$) ppm. ^{13}C NMR (100.4 MHz, DMSO-d_6): δ = 163.7, 155.8, 141.9, 140.5, 133.1, 131.7, 122.1, 119.6, 107.9, 63.3, 59.2, 54.9, 48.5, 35.1, 29.5, and 18.5 ppm. ^{27}Al NMR (104.3 MHz, DMSO-d_6): δ = 70.49 and 1.17 ppm. UV−vis: 353, 284, and 223 nm. Calcd for $C_{44}H_{58}AlI_2ClN_6O_2$ C, 51.85; H, 5.74; N, 8.25; Found: C, 51.78; H, 5.79; N, 8.21.

Complex ***2f***. IR 1636 ($\nu_{C=N}$), 1541 (Ph ving $\nu_{C=C}$), 1253 cm^{-1} (ν_{Ar-O}). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.35 (*s*, 2H, N=C), 7.41 (*s*, 2H, Ph-H), 7.37 (*s*, 2H, Ph-H), 3.16 (*m*,

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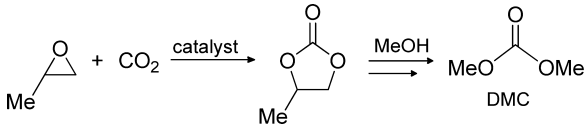
2H, CH-N), 1.62−1.96 (*m*, 4H, $(CH_2)_2$), 1.52(*s*, 18H, *t*-Bu), 1.28 (*s*, 18H, *tert*-Bu), and 0.85(*m*, 4H, $(CH_2)_2$) ppm. ^{13}C NMR (100.4 MHz, DMSO-d_6): δ = 164.0, 161.5, 138.9, 136.4, 129.2, 122.8, 118.8, 63.3, 48.6, 35.1, 33.7, 31.3, 29.8, 26.9, and 23.5 ppm. ^{27}Al NMR (104.3 MHz, DMSO-d_6): δ = 70.03 ppm. UV−vis: 361, 283, and 239 nm. Anal. Calcd for $C_{36}H_{52}AlClN_2O_2$ C, 71.20; H, 8.63; N, 4.44; Found: C, 71.18; H, 8.62; N, 4.49.

Synthesis of *N*-benzyl-4-(dimethylamino)pyridinium Chloride (BDAPC). A solution of benzyl chloride (1.38 g, 0.011 mol) in benzene (10 mL) was mixed with a solution of 4-(dimethylamino) pyridine (2.62 g, 0.010 mmol) and refluxed overnight. After cooling to room temperature, the white precipitate was collected by filtration. Yield: 85.6%. ^1H NMR (400 MHz, D_2O): δ = 8.05(*s*, 2H, CH of DMAP), 7.47(*s*, 3H, Ph−CH_2), 7.39(*s*, 2H, Ph−CH_2), 5.32(*s*, 4H, Ph−CH_2), and 3.20 (*s*, 6H, *N*-CH_3) ppm.

General Coupling Reaction of CO_2 and PO. The coupling reactions were carried out in a 100 mL stainless-steel autoclave equipped with a mechanical stirrer, which had been previously dried at 100 °C for 1 h under vacuum. In a typical reaction, the reactor was charged with appropriate amount of catalyst and epoxide. After the reactor was pressurized with CO_2 to a desired pressure, the reaction mixture was heated to temperature while stirring at about 200 rpm. Following reaction the reactor was cooled to ambient temperature, and the unreacted CO_2 was slowly released. The residuals were collected and distilled under vacuum. The resulting product was identified by ^1H NMR spectroscopy.

RESULTS AND DISCUSSION

Coupling Reactions of CO_2 and Epoxides. The salicylaldehydes employed in the salen(salen = *N*,*N*′-bis-(salicylidene)- cyclohexenediaminato) ligand synthesis were derived from 3-*tert*-butyl-5-bromomethyl-2- hydroxybenzaldehyde and the corresponding amine according to the route described by Jing and co-workers.[14] These salen ligands were used to prepare the single component bifunctional catalyst systems (**2a**−**2e**) by the method depicted in Scheme 1. Table 1 summarizes the coupling reactions of CO_2 with propylene oxide catalyzed by complexes (**2a**−**2e**) and the binary catalyst (**2f**) carried out under solventless conditions. The reaction conditions were specifically chosen to maximize formation of the cyclic carbonate. Herein, we have focused on the production of propylene carbonate since it and ethylene carbonate are precursors to the important organic carbonates, dimethyl carbonate and diphenyl carbonate, which serve as fuel additives or phosgene replacements (eq 2).



(2)

It is apparent from Table 1 that the one-component aluminum salen complexes (**2a**−**2d**) are all quite effective at catalyzing the cycloaddition of CO_2 and propylene oxide to propylene carbonate. As would be anticipated, the turnover frequencies (TOFs) are time-dependent, decreasing with longer reaction periods. In Table 1, it is also reported that complex **2f** or BDAPC alone (entries 4 and 9) are not very active for the cycloaddition reaction; however, together (entry 8) represent an efficient binary catalyst system for production of propylene carbonate. Nevertheless, this binary catalyst is significantly less active than all of its one-component analogues (entries 5−7 vs 8). This observation points out the positive effect on the catalytic process of incorporating the initiating anion and its countercation as part of the metal salen complex.

Furthermore, as noted in Table 1, changes in the nature of the cation from 4-dimethylaminopyridinium to pyridinium leads to a decrease in catalytic activity, presumably because of a decrease in acidity of the quaternary ammonium salt. At the same time maintaining the DMAP cation and varying the halide initiator illustrate the balance in nucleophilicity and leaving group ability of bromide as compared to the better nucleophile chloride and better leaving group iodide. A similar order of reactivity has been reported for CO_2/epoxide reactions catalyzed by tetrabutylammonium halides in the absence of a Lewis acid cocatalyst.[34] It is well-established that the role of the halide ion is to ring open the epoxide bound to the metal center to afford a halo-alkoxide intermediate which undergoes CO_2 insertion leading to a coordinated organic carbonate. Displacement of the halide by the carbonate to provide the cyclic carbonate follows. Hence, the catalytic effect of the halide is determined by a balance of its nucleophilicity and its leaving-group ability.

In an effort to gain insight into why the complexes with the appended onium salts (**2a**−**2c**, **2d**, and **2e**) were more effective as catalysts for the cycloaddition of epoxides and CO_2 relative to their binary catalyst analogues (**2f**/BDAPC), the samples were analyzed by ^{27}Al NMR spectroscopy. Because ^{27}Al NMR is sensitive to the symmetry, chemical environment, and coordination number around the metal center, this spectroscopic probe should be useful in assessing differences in these two different types of aluminum complexes.[35−39] ^{27}Al NMR spectra of complexes **2a**−**2e** were found to display broad strong resonances between 68.0 and 73.0 ppm and a weak signal in the range 0−13 ppm, while complex **2f** which lacks the attached quaternary ammonium salts on the ligand exhibits a single resonance at 70.03 ppm (Figure 2). Since an upfield chemical shift is attributed to an increase in aluminum's coordination number, the intense ^{27}Al resonance in complexes **2a**−**2e** and **2f** is assigned to the five-coordinate aluminum species and the weaker and more narrow upfield signal to a six-coordinate species.[40,41] Presumably, these two species are in equilibrium with one another, with the equilibrium position greatly favoring

Table 1. Coupling of CO_2 and PO Catalyzed by Various Catalysts

entry	catalyst[a]	time (h)	yield (%)[b]	TOF[c]
1	**2a**	5	74.3	297
2	**2b**	5	66.7	266
3	**2c**	5	51.1	204
4	**2f**	5	12.9	51
5	**2a**	2	65.0	650
6	**2d**	2	66.3	663
7	**2e**	2	44.2	442
8	**2f**/BDAPC	2	24.4	244
9	BDAPC	2	0.2	13.5

[a]Molar ratio of PO to complex **2a**−**f** = 2000:1 for entries 1−8, and **2f**:BDAPC = 1:2(molar ratio) in entry 8; while for entry 9 is 1000; Pressure: 3.0 MPa; complex: 3.5×10^{-2} mmol. Temperature: 120 °C. [b]PC obtained by distillation. [c]Turnover number for PC calculated as mole of PO consumed per mole of catalyst per hour.

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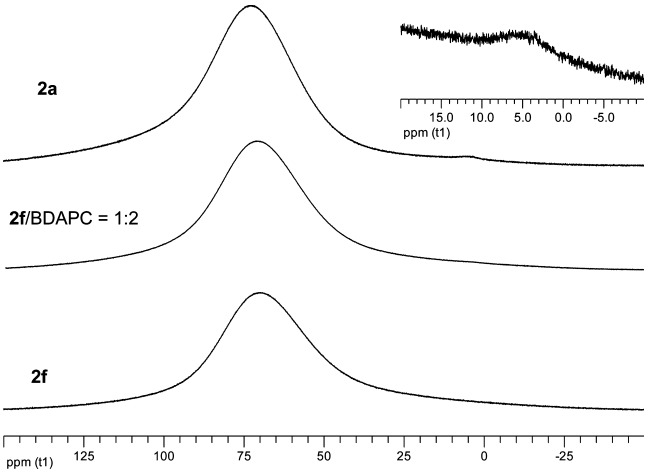


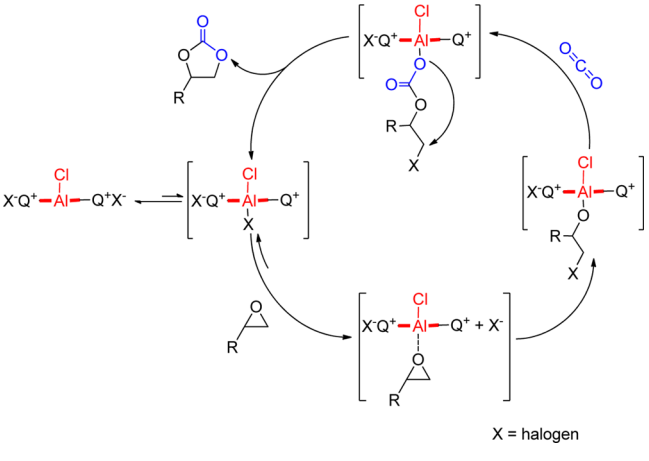
Figure 2. ^{27}Al NMR spectra of complex **2a**, **2f**, and mixture of **2f** and BDAPC in DMSO-d_6.

the five-coordinate complex. It is important to note as well in Figure 2 that complex **2f** in the presence of two equivalents of BDAPC displays only the five-coordinate aluminum complex.

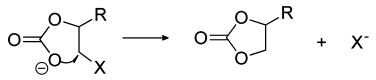
Hence, these observations are indicative of a more electrophilic aluminum center for complexes containing salen ligands with appended ammonium salts. Although it is surprising that the positive charge thought to be localized on the ammonium salt is somewhat perceived at the metal center, this phenomenon readily accounts for the enhanced catalytic activity observed for these derivatives. That is, in these instances the stronger Lewis acidity at the metal center binds the epoxide stronger and better activates it toward ring-opening by the halide anion.[42−44] In early studies, Inoue and co-workers observed a six-coordinate aluminum porphyrin complex in the presence of quaternary salts by UV−vis, infrared, and ^{1}H NMR spectroscopies.[45,46] These species existed in equilibrium with the five-coordinate complex and exhibited enhanced catalytic activity for the copolymerization of epoxides and acid anhydrides.

Scheme 2 outlines the proposed reaction pathway where the aluminum salen complexes containing the appended ammonium salts are more reactive than their binary catalyst analogues. These latter complexes in the presence of onium salts nevertheless catalyze the coupling of epoxides and CO_2 by the same pathway with the only difference being an

Scheme 2



enhancement of the rate determining ring-opening process for the one-component catalyst system.[47−50] Although the cyclization step following epoxide ring-opening and CO_2 insertion/addition is written in Scheme 2 as involving a metal bound carbonate species, this process most likely involves a nucleophilic displacement of the halide by a free organic carbonate anion (eq 3).[51]



(3)

The scope of this cycloaddition reaction was examined using complex **2a** and the epoxides, ethylene oxide, epichlorohydrin, and cyclohexene oxide with CO_2(3 MPa) at 120 °C for 2 h. Ethylene oxide and epichlorohydrin exhibited good reactivity with CO_2 to afford the corresponding cyclic carbonates under these conditions providing TOFs of 557 and 595 h^{-1}, respectively. This reactivity is comparable to that found for propylene oxide and CO_2 (650 h^{-1}) under similar reaction conditions. On the contrary, cyclohexene oxide showed poor reactivity with CO_2 to provide cyclic carbonate which is consistent with the high activation energy generally seen for this process.[51]

To optimize the reactivity of these single-component catalysts for the epoxide/CO_2 cycloaddition reaction, the influence of catalyst loading, reaction temperature, CO_2 pressure, and reaction time was investigated utilizing complex **2a**. These studies are summarized in Table 2. As noted in Table

Table 2. Coupling of CO_2 and PO Catalyzed by Complex 2a at Various Reaction Conditions

entry	PO/**2a**[a]	pressure (Mpa)	temp (°C)	time (h)	yield[b] (%)	TOF[c]
1	2000:1	2.0	100	2	55.5	555
2	2000:1	2.0	120	2	58.9	589
3	2000:1	2.0	140	2	62.7	627
4	2000:1	1.5	120	2	51.3	513
5	2000:1	2.3	120	2	60.3	603
6	2000:1	3.0	120	2	65.0	650
7	4000:1	3.0	120	2	41.5	830
8	6000:1	3.0	120	2	29.1	873
9	8000:1	3.0	120	2	18.3	732
10	6000:1	3.0	120	3	40.8	817
11	6000:1	3.0	120	4	49.6	744

[a]Complex **2a**: 3.5 × 10−2 mmol. [b]PC obtained by distillation. [c]Turnover number for PC calculated as mole of PO consumed per mole of catalyst per hour.

2, there was a modest increase in catalytic activity upon increasing the CO_2 pressure from 1.5 MPa (513 h^{-1}) to 3.0 MPa (650 h^{-1}) (entries 4−6). Importantly, the TOFs were shown not to decrease upon reducing the catalyst loading (entries 6−9). This is in general a positive feature of catalyst systems where the onium salt initiator is appended to the salen ligand as compared to their binary catalyst counterparts. Furthermore, these one-component catalysts were found to be stable over longer reaction times and higher temperatures. That is, the yield of propylene carbonate steadily increased from 29.1−49.6% over a 4 h period (entries 8, 10, and 11), and the

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complex exhibited high thermal stability over the temperature range 100−140 °C (entries 1−3).

An important additional feature for any catalyst system designed for large scale production of commodity chemicals such as cyclic organic carbonates is their *reusability without significant loss in catalytic activity*. To examine this characteristic of these catalysts, the synthesis of propylene carbonate was carried out for 1 h at 120 °C and 3.0 MPa of CO_2 at a molar ratio of PO/catalyst of 500 employing complex **2a**. Following each cycle, the catalyst was recovered by distillation to dryness of the volatiles and reused for a new batch reaction under identical reaction conditions. The results of five reaction cycles are displayed in Figure 3, where no significant loss in catalytic activity was noted. In addition, this catalyst exhibited stability to moisture. For example, complex **2a** was immersed in distilled water overnight at ambient temperature. Following drying, complex **2a** maintained its catalytic activity, displaying a TOF of 646 h^{-1} for the production of propylene carbonate under the reaction conditions of entry 5 in Table 1 which showed a TOF of 650 h^{-1}. In this regard, it should also be noted that no special precautions were taken to purify either propylene oxide or CO_2. These considerations are of utmost importance when utilizing impure sources of CO_2 as that obtained from power plant flue gases or exhaust streams from chemical plants or other CO_2 producers.

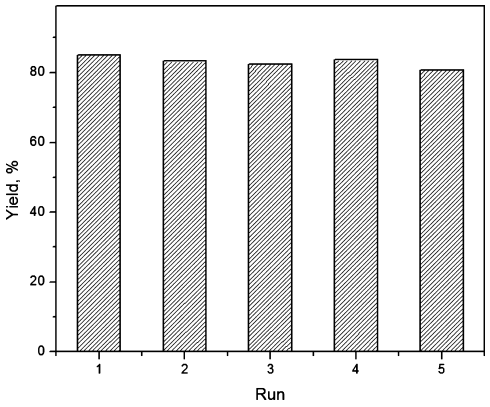

Figure 3. Isolated yields of propylene carbonate produced using recycled catalyst **2a**. Reaction conditions were 1 h at 120 °C and 3 MPa CO_2 with a PO/catalyst loading of 500/1.

CONCLUDING REMARKS

Several new (salen)AlCl derivatives bearing quaternary ammonium salts bound to the 3-position of the salen's ligand phenyl rings have been prepared and examined for their effectiveness as single-component catalysts for the cycloaddition of epoxides and CO_2 to provide cyclic organic carbonates. These complexes were significantly more efficient at catalyzing this process than their binary metal analogues. This enhanced catalytic activity was attributed to the aluminum center being more electrophilic in the case of the complexes with the appended ammonium salts, an observation supported by ^{27}Al NMR studies. These bifunctional aluminum catalysts have many merits in common with (salen)CoX catalysts similarly containing attached onium salts. However, in these instances where six-coordination complexes are favored, the effect is ascribed to the cation maintaining interactions with the growing anionic polymer chain to limit the backbiting reaction of the free copolymer chain leading to cyclic carbonate production. In the case of the (salen)AlCl catalysts where five-coordinate complexes are favored, the role of the appended onium salt is to enhance the electrophilicity of the aluminum center leading to greater epoxide activation. Indeed, this latter phenomenon might account in part for the enhanced selectivity for copolymer formation in the (salen)CoX reactions. These newly synthesized (salen)AlCl catalysts also possess the desirable attributes of being effective at low catalyst loading, being thermally and moisture stable, and being recyclable without significant loss in catalytic activity.

In general, it is hard to critically compare the efficacy of the numerous catalyst systems for the coupling of epoxides and CO_2 to produce cyclic carbonates because of the wide variation in reaction conditions. Nevertheless, the aluminum catalysts reported upon herein are competitive with most catalysts currently available, including transition and main group metals as well as organo-catalysts. This is especially true when one considers their ease and effectiveness for recycling. See, for example, the extensive summary of catalysts and their activities for this process in the recent review by Omae.[52]

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Notes

The authors declare no competing financial interest.

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