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Aluminum Salen Complexes and Tetrabutylammonium Salts: A Binary Catalytic System for Production of Polycarbonates from CO_2 and Cyclohexene Oxide

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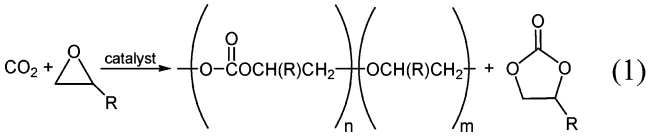
A series of complexes of the form (salen)AlZ, where H_2salen = *N*,*N*′-bis(salicylidene)-1,2-phenylenediimine and various other salen derivatives and Z = Et or Cl, have been synthesized. Several of these complexes have been characterized by X-ray crystallography. An investigation of the utilization of these aluminum derivatives along with both ionic and neutral bases as cocatalysts for the copolymerization of carbon dioxide and cyclohexene oxide has been conducted. By studying the reactivity of these complexes for this process as substituents on the diimine backbone and phenolate rings are altered, we have observed that aluminum prefers electron-withdrawing groups on the salen ligands, thereby producing an electrophilic metal center to be most active toward production of polycarbonates from CO_2 and cyclohexene oxide. For example, the complex derived from H_2salen = *N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine is essentially inactive when compared to the analogous derivative containing nitro substituents in the 3-positions of the phenolate groups. This is to be contrasted with the catalytic activity observed for the (salen)CrX systems, where electron-donating salen ligands greatly enhanced the reactivity of these complexes for the coupling of CO_2 and epoxides. While (salen)AlZ complexes are capable of producing poly(cyclohexene oxide) carbonate with low amounts of polyether linkage along with small quantities of cyclic carbonate byproducts, their reactivities, covering a turnover frequency range of 5.2–35.4 mol of epoxide consumed/(mol of Al•h), are greatly reduced when compared to their (salen)CrX analogues under identical reaction conditions.

Introduction

Both transition and main group metal porphyrin derivatives have been employed as catalysts for the coupling of carbon dioxide and epoxides to provide polycarbonates and/or cyclic carbonates (eq 1). Notably, these complexes are structurally similar to the magnesium-containing porphyrin species used in photosynthesis, chlorophyll. Prominent among these reports are the pioneering investigations of Inoue and co-workers[1] and the more recent efforts of Kruper,[2] Holmes,[3] and Chisholm.[4] During this same time period we and others have utilized various *salen* (bis(salicylaldiimine)) ligands which afford similar transition metal complexes which serve as effective catalysts for this process.[5] These latter ligands represent less expensive, more easily derivatized alternatives to porphyrin ligands.



We have recently been interested in examining the utilization of salen complexes of main group metals as catalysts for reaction 1. Our initial attempts at the use of gallium salen complexes were unsuccessful in producing polycarbonate.[6] Given the success demonstrated by aluminum porphryinates at production of polycarbonates,[1,4] we have undertaken investigations into the use of salen aluminum derivatives as catalysts for this process. These efforts are designed to optimize the effectiveness of these aluminum reagents by systematic variation of the electronics of the salen ligand and

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the nature of the cocatalyst, much as we have accomplished with the chromium derivatives.[7,8] Indeed, the latest elegant mechanistic studies reported by Chisholm and Zhou attest to the many similarities in the details of the reaction pathways for the CO_2/epoxide coupling reaction catalyzed by aluminum porphyrin and chromium salen derivatives.[4] Of some consideration is the fact that these aluminum complexes are expected to be much less toxic than their chromium analogues.

Experimental Section

Methods and Materials. All manipulations were performed using a combination of standard Schlenk and drybox techniques. Toluene and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone prior to use. Acetonitrile was first dried by distillation from CaH_2 onto P_2O_5 followed by distillation onto CaH_2 and then freshly distilled from CaH_2 prior to use. Cyclohexene oxide (CHO) was distilled from CaH_2 prior to use. CH_2Cl_2 was freshly distilled from P_2O_5 prior to use. Methanol and ethanol were distilled from the corresponding magnesium alkoxide prior to use. Bone dry CO_2 was purchased from Scott Specialty Gases. $AlEt_3$ and Et_2AlCl were purchased from Aldrich as 1.9 M toluene solutions and used as received. Salicylaldehyde, ethylenediamine, and 1,2-phenylenediamine were purchased from Aldrich and used as received. Cyclohexyldiamine was purchased as a mixture of trans and cis isomers from Aldrich and used as received. 2,4,6-Trimethylphenol and phenol were purchased from Aldrich and sublimed prior to use. 3,5-Di-*tert*-butylsalicylaldehyde and 3-*tert*-butyl-5-nitrosalicylaldehyde were prepared according to literature procedures.[9] Synthesis of the ligands *N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-ethylenediimine [(^{t}Bu)$_2$salenH$_2$],[10d] *N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-*R*,*R*-cyclohexyldiimine [(cyc)(^{t}Bu)$_2$salenH$_2$],[10c] *N*,*N*′-bis(salicylaldehyde)-1,2-phenylenediimine [(phen)salenH$_2$],[10b] *N*,*N*′-bis(3,5-dichlorosalicylidene)-1,2-ethylenediimine [(Cl$_2$)salenH$_2$],[10e] *N*,*N*′-bis(3,5-dichlorosalicylidene)-1,2-phenylenediimine [(phen)(Cl$_2$)salenH$_2$],[10a] and *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediimine [(phen)(^{t}Bu)$_2$salenH$_2$][10f] were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on Unity+ 300 MHz and VXR 300 MHz superconducting NMR spectrometers. The operating frequency for ^{13}C NMR experiments was 75.41 MHz. Infrared spectra were recorded on a Mattson 6021 FT-IR spectrometer with DTGS and MCT detectors. Analytical elemental analysis was provided by Canadian Microanalytical Services Ltd.

Synthesis of *N*,*N*′-Bis(3-*tert*-butyl-5-nitrosalicylidene)-1,2-ethylenediamine [(^{t}Bu)(NO$_2$)salenH$_2$] (1). 3-*tert*-Butyl-5-nitrosalicylaldehyde (2.0 g, 8.96 mmol) was dissolved in 40 mL of ethanol in a 250 mL round-bottom flask fitted with a reflux condenser. Ethylenediamine (0.360 g, 4.48 mmol) in 10 mL of ethanol was added along with 1 drop of formic acid and the condenser washed with 10 mL of ethanol. Immediate formation of a dark yellow precipitate was observed. The mixture was allowed to reflux for 4 h, cooled, and placed in a freezer at −30 °C for 12 h. The resultant yellow solid was collected by filtration, washed with cold ethanol (2 × 20 mL), and dried under vacuum to yield 1.5 g (71%) of dark yellow powder. X-ray-quality crystals were grown by slow evaporation of a concentrated CH_2Cl_2 solution. ^{1}H NMR (C_6D_6): δ = 1.07 [s, 18H, C(*CH*$_3$)$_3$], 2.62 [s, 4H, N*CH*$_2$*CH*$_2$N], 6.89 [s, 2H, phenyl-*H*], 7.55 [s, 2H, phenyl-*H*], 7.99 [s, 2H, phenyl-*CH*═N], 14.78 [s, 2H, −*OH*]. ^{13}C NMR (C_6D_6): δ = 28.83, 35.22, 57.68, 125.34, 126.30, 166.35. Anal. Calcd for $C_{24}H_{30}N_4O_6$: C, 60.26; H, 6.43; N, 11.9. Found: C, 59.77; H, 6.41; N, 11.14.

Synthesis of *N*,*N*′-Bis(3-*tert*-butyl-5-nitrosalicylidene)-1,2-phenylenediamine [(phen)(^{t}Bu)(NO$_2$)salenH$_2$] (2). A 250 mL round-bottom flask was charged with 3-*tert*-butyl-5-nitrosalicylaldehyde (3.2 g, 14.3 mmol) and 50 mL of dry ethanol. A 25 mL ethanol slurry of 1,2-phenylenediamine (0.775 g, 7.15 mmol) and 2 drops of formic acid were added. The immediate formation of an orange precipitate is observed. The flask was fitted with a reflux condenser and the mixture refluxed for 2 h. The mixture was cooled to −30 °C overnight. The orange precipitate was collected by filtration and washed with cold ethanol (2 × 20 mL) to yield 4.78 g of orange powder (60%). ^{1}H NMR (C_6D_6): δ = 1.40 [s, 18H, C(*CH*$_3$)$_3$], 6.62−6.65 [m, 2H, N-phenyl-*H*], 6.99−7.00 [m, 2H, N-phenyl-*H*], 7.61 [s, 2H, phenyl-*H*], 7.78 [d (J_H-J_H, 2.4 Hz), 2H, phenyl-*H*], 8.32 [d (J_H-J_H, 0.3 Hz), 2H, phenyl-*CH*═N], 14.80 [s, 2H, −*OH*]. ^{13}C NMR (C_6D_6): δ = 1.26, 28.88, 119.66, 125.79, 127.08, 162.93. Anal. Calcd for $C_{28}H_{30}N_4O_6$: C, 64.85; H, 5.83; N, 10.8. Found: C, 62.92; H, 4.32; N, 9.66.

Synthesis of *N*,*N*′-Bis(3-*tert*-butyl-5-nitrosalicylidene)-1,2-ethylenediamine [(^{t}Bu)(NO$_2$)salenH$_2$] (1). 3-*tert*-Butyl-5-nitrosalicylaldehyde (2.0 g, 8.96 mmol) was dissolved in 40 mL of ethanol in a 250 mL round-bottom flask fitted with a reflux condenser. Ethylenediamine (0.360 g, 4.48 mmol) in 10 mL of ethanol was added along with 1 drop of formic acid and the condenser washed with 10 mL of ethanol. Immediate formation of a dark yellow precipitate was observed. The mixture was allowed to reflux for 4 h, cooled, and placed in a freezer at −30 °C for 12 h. The resultant yellow solid was collected by filtration, washed with cold ethanol (2 × 20 mL), and dried under vacuum to yield 1.5 g (71%) of dark yellow powder. X-ray-quality crystals were grown by slow evaporation of a concentrated CH_2Cl_2 solution. ^{1}H NMR (C_6D_6): δ = 1.07 [s, 18H, C(*CH*$_3$)$_3$], 2.62 [s, 4H, N*CH*$_2$*CH*$_2$N], 6.89 [s, 2H, phenyl-*H*], 7.55 [s, 2H, phenyl-*H*], 7.99 [s, 2H, phenyl-*CH*═N], 14.78[s, 2H, −*OH*]. ^{13}C NMR (C_6D_6): δ = 28.83, 35.22, 57.68, 125.34, 126.30, 166.35. Anal. Calcd for $C_{24}H_{30}N_4O_6$: C, 60.26; H, 6.43; N, 11.9. Found: C, 59.77; H, 6.41; N, 11.14.

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Synthesis of *N,N′*-Bis(3-*tert*-butyl-5-nitrosalicylidene)-1,2-phenylenediamine [(phen)(^{t}Bu)(NO_2)salenH_2] (2). A 250 mL round-bottom flask was charged with 3-*tert*-butyl-5-nitrosalicylaldehyde (3.2 g, 14.3 mmol) and 50 mL of dry ethanol. A 25 mL ethanol slurry of 1,2-phenylenediamine (0.775 g, 7.15 mmol) and 2 drops of formic acid were added. The immediate formation of an orange precipitate was observed. The flask was fitted with a reflux condenser and the mixture refluxed for 2 h. The mixture was cooled to −30 °C overnight. The orange precipitate was collected by filtration and washed with cold ethanol (2 × 20 mL) to yield 4.78 g of orange powder (60%). ^{1}H NMR (C_6D_6): δ = 1.40 [s, 18H, C(CH_3)$_3$], 6.62−6.65 [m, 2H, N-phenyl-*H*], 6.99−7.00 [m, 2H, N-phenyl-*H*], 7.61 [s, 2H, phenyl-*H*], 7.78 [d (J_H−J_H, 2.4 Hz), 2H, phenyl-*H*], 8.32 [d (J_H−J_H, 0.3 Hz), 2H, phenyl-*CH*═N], 14.80 [s, 2H, −*OH*]. ^{13}C NMR (C_6D_6): δ = 1.26, 28.88, 119.66, 125.79, 127.08, 162.93. Anal. Calcd for $C_{28}H_{30}N_4O_6$: C, 64.85; H, 5.83; N, 10.8. Found: C, 62.92; H, 4.32; N, 9.66.

Synthesis of {salen}Al^{III}Et Complexes. The synthesis of {salen}AlEt complexes was performed via one of two methods: A or B.

Method A. This procedure is an adaptation of procedures described in the literature by Atwood et al.[11] A 100 mL Schlenk flask fitted with a reflux condenser was charged with salenH_2 and 30 mL of toluene. A 50 mL Schlenk flask was charged with 1 equiv of a 1.9 M toluene solution of $AlEt_3$. An additional 10 mL of toluene was added, and the solution was cannulated onto the ligand mixture. The reflux condenser was washed with 5 mL of toluene. The mixture was stirred under reflux for 1 h, cooled, and stirred at room temperature for 1 h. The solvent was removed under reduced pressure.

Method B. This procedure is an adaptation of a procedure described in the literature by Dzugan and Goedken.[12] A 50 mL Schlenk flask was charged with salenH_2 in 30 mL of CH_3CN. A second 50 mL Schlenk flask was charged with 1 equiv of a 1.9 M toluene solution of $AlEt_3$. A 10 mL volume of CH_3CN was added, and the solution was cannulated onto the ligand mixture. The mixture was stirred at room temperature 2 h and the solvent removed under reduced pressure.

Synthesis of {*N,N′*-Bis(3-*tert*-butyl-5-nitrosalicylidene)-1,2-ethylenediamine}aluminum(III) Ethyl [{(^{t}Bu)(NO_2)salen}AlEt] (1b). Method A was followed with (^{t}Bu)(NO_2)salenH_2 (0.471 g, 1.0 mmol) and 0.53 mL (1.0 mmol) of a 1.9 M toluene solution of $AlEt_3$. The immediate formation of a dark orange-red solution was observed. The solvent was removed under reduced pressure to yield 0.448 g (85%) of orange powder. ^{1}H NMR ($CDCl_3$): δ = −0.31 [q (J_H−J_H, 8.1 Hz), 2H, AlCH_2CH$_3$], 0.72 [t (J_H−J_H, 8.1 Hz), 3H, AlCH$_2$CH_3], 1.51 [s, 18H, C(CH_3)], 3.90−3.93 [m, 2H, NCH_2-CH_2N], 4.08−4.17 [m, 2H, NCH$_2$CH_2N], 8.18 [s, 2H, phenyl-*H*], 8.35 [s, 2H, phenyl-*H*], 8.50 [s, 2H, phenyl-C*H*═N]. Anal. Calcd for $C_{24}H_{33}N_4O_6Al$: C, 58.53; H, 6.34; N, 10.68. Found: C, 57.68; H, 6.13; N, 9.84.

Synthesis of {*N,N′*-Bis(3-*tert*-butyl-5-nitrosalicylidene)-1,2-phenylenediamine}aluminum(III) Ethyl [{(phen)(^{t}Bu)(NO_2)-salen}AlEt] (2b). Method B was followed with (phen)(^{t}Bu)(NO_2)-salenH_2 (0.250 g, 0.54 mmol) and $AlEt_3$ (0.30 mL of a 1.9 M toluene solution, 0.54 mmol). This yields 0.253 g of reddish-brown powder (82%). ^{1}H NMR (DMSO-d_6): δ = −0.53 [q (J_H−J_H, 8.1 Hz), 2H, AlCH_2CH$_3$], 0.48 [t (J_H−J_H, 8.1 Hz), 3H, AlCH$_2$CH_3], 1.53 [s, 18H, C(CH_3)], 8.13−8.20 [m, 4H, N-phenyl-*H*], 8.60 [s, 2H, phenyl-*H*], 9.35 [s, 2H, phenyl-*H*], 9.62 [s, 2H, phenyl-C*H*═N]. Anal. Calcd for $C_{30}H_{33}N_4O_6Al$: C, 61.93; H, 5.81; N, 9.78. Found: C, 60.76; H, 6.40; N, 9.09.

Synthesis of {*N,N′*-Bis(3,5-dichlorosalicylidene)-1,2-ethylenediamine}aluminum(III) Ethyl [{(Cl_2)salen}AlEt] (3). Method A was followed with (Cl_2)salenH_2 (0.585 g, 1.4 mmol) and $AlEt_3$ (0.737 mL of a 1.5 M toluene solution, 1.4 mmol). This yielded 0.588 g (90%) of a bright yellow powder. ^{1}H NMR (DMSO-d_6): δ = −0.58 [q (J_H−J_H, 7.8 Hz), 2H, AlCH_2CH$_3$], 0.63 [t (J_H−J_H, 8.1 Hz), 3H, AlCH$_2$CH_3], 3.91 [s, 2H, NCH_2CH_2N], 7.20−7.71 [m, 4H, phenyl-C*H*], 8.58 [s, 2H, phenyl-C*H*═N]. Anal. Calcd for $C_{18}H_{15}N_2O_2AlCl_4$: C, 46.99; H, 3.29; N,6.09. Found: C, 45.61; H, 3.88; N, 5.33.

Synthesis of {*N,N′*-Bis(salicylidene)-1,2-phenylenediamine}-aluminum(III) Ethyl [(phen)salenAlEt] (4). The procedure described by Dzugan and Goedken was followed. Spectroscopic measurements were in agreement with the literature.[12]

Synthesis of {*N,N′*-Bis(3,5-dichlorosalicylidene)-1,2-phenylenediamine}aluminum(III) Ethyl [{(phen)Cl_2salen}AlEt] (5). Method B was followed with (phen)Cl_2salenH_2 (0.454 g, 1.0 mmol) and 0.53 mL (1.0 mmol) of a 1.9 M toluene solution of $AlEt_3$. The immediate formation of a dark orange-red solution was observed. The mixture was stirred at room temperature 2 h, and an orange precipitate began to form. The solution was concentrated under reduced pressure to ∼10 mL, and 30 mL of hexanes was added to completely precipitate the product. The precipitate was collected by filtration and dried under vacuum to yield 0.420 g (87%) of orange powder. ^{1}H NMR (DMSO-d_6): δ = −0.71 [q (J_H−J_H, 8.1 Hz), 2H, AlCH_2CH$_3$], 0.47 [t (J_H−J_H, 8.1 Hz), 3H, AlCH$_2$CH_3], 7.55−7.59 [m, 2H, N-phenyl-C*H*], 7.65 [d, 2H, phenyl-C*H*], 7.70 [s, 2H, phenyl-C*H*], 8.00−8.03 [m, 2H, N-phenyl-C*H*], 9.16 [s, 2H, phenyl-C*H*═N]. Anal. Calcd for $C_{22}H_{15}N_2O_2AlCl_4$: C, 52.00; H, 2.98; N, 5.51. Found: C, 51.92; H, 3.05; N, 6.12.

Synthesis of {*N,N′*-Bis(5-nitrosalicylidene)-1,2-ethylenediamine}aluminum(III) Ethyl (6). Method A was followed with (NO_2)salenH_2 (0.359 g, 1.0 mmol) and $AlEt_3$ (0.55 mL of a 1.5 M toluene solution, 1.0 mmol). This yielded 0.303 g (73%) of pale yellow powder. ^{1}H NMR (DMSO-d_6): δ = −0.599 [q (J_H−J_H, 8.1 Hz), 2H, Al−CH_2CH$_3$], 0.614 [t (J_H−J_H, 8.1 Hz), 3H, Al−CH$_2$CH_3], 3.81−4.02 [m, 4H, NCH_2CH_2N], 6.87−6.90 [d, 2H, phenyl-*H*], 8.13−8.17 [m, 2H, phenyl-*H*], 8.42−8.43 [d, 2H, phenyl-*H*], 8.70 [s, 2H, phenyl-C*H*═N].

Synthesis of {*N,N′*-Bis(3,5-di-*tert*-butylsalicylidene)-*R,R*-cyclohexyldiimine}aluminum(III) Ethyl [{(cyc)(^{t}Bu)$_2$salen}AlEt] (7). This was prepared as described in the literature. Spectroscopic data were in accordance with those reported.[13]

Synthesis of {salen}AlCl. The syntheses of {salen}AlCl complexes are adaptations of the procedure described by Rutherford and Atwood in the literature.[14] Further experimental details are given below.

Synthesis of {*N,N′*-Bis(3-*tert*-butyl-5-nitrosalicylidene)-1,2-ethylenediamine}aluminum(III) Chloride [{(^{t}Bu)(NO_2)salen}-AlCl] (1c). A 50 mL Schlenk flask was charged with (^{t}Bu)(NO_2)-salenH_2 (0.471 g, 1.0 mmol), which was then dissolved in 40 mL of toluene. A 100 mL Schlenk flask was charged with 0.53 mL (1.0 mmol) of a 1.9 M toluene solution of Et_2AlCl, and an additional 10 mL of toluene was added. The ligand was cannulated into the flask containing the metal, and the mixture was stirred for 12 h at room temperature. A yellow precipitate was observed. The reaction

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mixture was concentrated to ~10 mL, and 30 mL of hexanes was added to precipitate the product. The precipitate was collected by filtration and dried under vacuum to yield 0.480 g (91%) of yellow powder. ^{1}H NMR(DMSO-d_6): δ = 1.53 [s, 18H, C(CH_3)$_3$], 3.96 [s, 4H, NCH_2CH_2N], 8.18−8.19 [d, 2H, phenyl-*H*], 8.45−8.46 [d, 2H, phenyl-*H*], 8.81 [s, 2H, phenyl-C*H*═N]. Anal. Calcd for $C_{24}H_{28}N_4O_6AlCl$: C, 54.29; H, 5.32; N, 10.55. Found: C, 54.24; H, 5.48; N, 10.16.

Synthesis of {*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamine}aluminum(III) Chloride [{(^{t}Bu)$_2$salen}AlCl] (8). This was prepared according to the literature procedure. Yield and spectroscopic data were in accordance with those reported in the literature.[14]

Synthesis of {*N*,*N*′-Bis(3,5-dichlorosalicylidene)-1,2-ethylenediamine}aluminum(III) Chloride [{Cl$_2$salen}AlCl] (9). A 50 mL Schlenk flask was charged with Cl$_2$salenH$_2$ (0.219 g, 0.54 mmol), which was then dissolved in 40 mL of toluene. A 100 mL Schlenk flask was charged with 0.30 mL (1.0 mmol) of a 1.9 M toluene solution of Et$_2$AlCl, and an additional 10 mL of toluene was added. The ligand was cannulated into the flask containing the metal, and the mixture was stirred for 12 h at room temperature. A yellow precipitate was observed. The reaction mixture was concentrated to ~10 mL, and 30 mL of hexanes was added to precipitate the product. The precipitate was collected by filtration and dried under vacuum to yield 0.224 g (89%) of yellow powder. ^{1}H NMR (DMSO-d_6): δ = 3.91 [s, 4H, NCH_2CH_2N], 7.56−7.57 [m, 2H, phenyl-*H*], 7.69−7.72 [m, 2H, phenyl-*H*], 8.60 [s, 2H, phenyl-C*H*═N].

Synthesis of {*N*,*N*′-Bis(salicylidene)-1,2-phenylenediamine}-aluminum(III) Chloride [{(phen)salen}AlCl] (10). A 50 mL Schlenk flask was charged with (phen)salenH$_2$ (0.454 g, 1.0 mmol), which was then dissolved in 30 mL of CH$_3$CN. A 50 mL Schlenk flask was charged with 0.53 mL (1.0 mmol) of a 1.9 M toluene solution of Et$_2$AlCl. A 10 mL volume of CH$_3$CN was added, and the solution was cannulated onto the ligand mixture. The immediate formation of a dark orange-red solution was observed. The mixture was stirred at room temperature 2 h, and an orange precipitate began to form. The solution was concentrated under reduced pressure to ~10 mL, and 30 mL of hexanes was added to completely precipitate the product. The precipitate was collected by filtration and dried under vacuum to yield 0.420 g (87%) of orange powder. ^{1}H NMR (DMSO-d_6): δ = 6.81 [t (J_H−J_H, 7.8 Hz), 2H, phenyl-*H*], 6.95 [d, 2H, phenyl-*H*], 7.49−7.54 [m, 4H, N-phenyl-*H*], 7.69 [d, 2H, phenyl-*H*], 8.15−8.18 [m, 2H, phenyl-*H*], 9.34 [s, 2H, phenyl-C*H*═N]. Anal. Calcd for $C_{16}H_{10}N_2O_2AlCl_5$: C, 41.19; H, 2.16; N, 6.00. Found: C, 40.29; H, 2.19; N, 5.40.

Synthesis of {*N*,*N*′-Bis(3,5-dichlorosalicylidene)-1,2-phenylenediamine}aluminum(III) Chloride [{(phen)Cl$_2$salen}AlCl] (11). A 50 mL Schlenk flask was charged with (phen)Cl$_2$salenH$_2$ (0.250 g, 0.55 mmol), which was then dissolved in 30 mL of CH$_3$CN. A 50 mL Schlenk flask was charged with 0.31 mL (0.55 mmol) of a 1.9 M toluene solution of Et$_2$AlCl. A 10 mL volume of CH$_3$CN was added, and the solution was cannulated onto the ligand mixture. The immediate formation of an orange-yellow precipitate was observed. The mixture was stirred at room temperature 2 h and concentrated under reduced pressure to ~10 mL, and 30 mL of hexanes was added to completely precipitate the product. The precipitate was collected by filtration and dried under vacuum to yield 0.235 g (83%) of yellow powder. ^{1}H NMR (DMSO-d_6): δ = 7.57−7.72 [m, 4H, N-phenyl-*H*], 7.97 [s, 2H, phenyl-*H*], 8.29 [s, 2H, phenyl-*H*], 9.64 [s, 2H, phenyl-C*H*═N]. Anal.

Synthesis of {*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine}aluminum(III) Chloride [{(phen)(^{t}Bu)$_2$salen}-AlCl] (12). This was prepared according to the literature procedure. Yield and spectroscopic data were in accordance with those reported in the literature.[14]

Synthesis of {*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamine}aluminum(III) 2,4,6-Trimethylphenoxide [{(^{t}Bu)$_2$salen}Al(OC$_6$H$_2$(CH$_3$)$_3$)] (13). A 100 mL Schlenk flask fitted with a reflux condenser was charged with (^{t}Bu)$_2$salenH$_2$ (0.500 g, 1.0 mmol), which was then dissolved in 30 mL of toluene. A 50 mL Schlenk flask was charged with 0.53 mL (1.0 mmol) of a 1.9 M toluene solution of AlEt$_3$. An additional 10 mL of toluene was added, and the solution was cannulated onto the ligand mixture. The reflux condenser was washed with 5 mL of toluene. The mixture was stirred under reflux 1 h, cooled, and stirred at room temperature 1 h to yield a bright yellow solution. A 10 mL toluene solution of 2,4,6-trimethylphenol was added and the mixture stirred 1 h. The solution was concentrated to ~10 mL, and 30 mL hexanes was added to precipitate the product. The precipitate was collected by filtration and dried under vacuum to yield 0.340 g (52%) of a yellow powder. ^{1}H NMR (C_6D_6): δ = 1.37 [s, 18H, C(CH_3)$_3$], 1.79 [s, 18H, C(CH_3)$_3$], 2.02 [s, 6H, phenoxide-CH_3], 2.17 [s, 3H, phenoxide-CH_3], 2.54−2.63 [m, 2H, NCH_2CH$_2$N], 3.22−3.29 [m, 2H, NCH$_2$CH_2N], 6.72 [s, 2H, phenoxide-CH_2], 6.95−6.96 [d (J_H−J_H, 2.4 Hz), 2H, phenyl-C*H*], 7.46 [s, 2H, phenyl-CH_2], 7.78 [d (J_H−J_H, 2.5 Hz), 2H, phenyl-C*H*═N]. Anal. Calcd for $C_{41}H_{57}N_2O_3Al$: C, 75.43; H, 8.80; N, 4.29. Found: C, 75.12; H, 8.94; N, 4.59.

Synthesis of {*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamine}aluminum(III) Phenoxide [{(^{t}Bu)$_2$salen}Al(OPh)] (14). The method described above was repeated using (^{t}Bu)$_2$salen}-H$_2$ (0.374 g, 0.76 mmol), AlEt$_3$ (0.400 mL, 0.76 mmol), and phenol (0.072 g, 0.76 mmol). This yielded 0.328 g (71%) of a bright yellow powder. ^{1}H NMR (C_6D_6): δ = 1.39 [s, 18H, C(CH_3)$_3$], 1.83 [s, 18H, C(CH_3)$_3$], 2.51−2.60 [m, 2H, NCH_2CH$_2$N], 3.15−3.24 [m, 2H, NCH$_2$CH_2N], 6.68−6.70 [m, 2H, phenoxide-*H*], 6.73−6.78 [m, 2H, phenoxide-*H*], 6.95−6.96 [m, 2H, phenyl-*H*], 7.48 [s, 2H, phenyl-*H*], 7.78−7.79 [m, 2H, phenyl-C*H*═N].

Copolymerization of Epoxides and CO$_2$. (salen)AlZ (50 mg) and the corresponding cocatalyst were dissolved in 20 mL of neat epoxide. The solution was added via injection port into a 300 mL Parr autoclave previously dried in vacuo at 80 °C overnight. The autoclave was charged with 500 psi CO$_2$ and maintained at 80 °C for a period of 8 h. The autoclave was then cooled to room temperature and vented in a fume hood. The polymer was extracted with dichloromethane and dried under vacuum at 100 °C for a period of 6 h.

The collected polycarbonate was analyzed by ^{1}H NMR, where the amount of ether linkages was determined by integrating the peaks corresponding to the methane protons of polyether at ~3.45 ppm and polycarbonate at ~4.6 ppm. Further analysis was done by infrared spectroscopy to identify monomeric *trans*-cyclohexyl carbonate with ν(C═O) at 1825 cm^{-1} or *cis*-cyclohexyl carbonate with ν(C═O) at 1804 cm^{-1}. The percentage of *trans*-cyclohexyl carbonate relative to copolymer was determined by integrating the ^{1}H NMR peaks corresponding to the methane protons of the polymer at ~4.6 ppm and *trans*-cyclohexyl carbonate at ~4.0 ppm.

High-Pressure in Situ Kinetic Measurements. High-pressure kinetic measurements were carried out using a stainless steel Parr autoclave modified with a SiComp window to allow for attenuated total reflectance spectroscopy using infrared radiation (ASI ReactIR 1000 in situ probe). After the autoclave was dried in vacuo overnight at 80 °C, 10 mL of neat epoxide was loaded via injection port. After the background solvent reached 80 °C, a single 128-scan background was collected. The desired catalyst and tetrabutylammonium salt cocatalyst were dissolved in 10 mL of neat epoxide

and injected into the autoclave followed by immediate charging with 50 bar of CO_2 pressure. With maintenance of a reaction temperature of 80 °C, a single 128-scan spectrum was collected every 3 min for 10 h. Profiles of the absorbance at 1750 cm^{-1} (polycarbonate) and ~1825 cm^{-1} (cyclic carbonate) versus time were recorded after baseline correction. After the sample was cooled and vented in a fume hood, the polymer was extracted as a dichloromethane solution and dried under vacuum at 100 °C overnight. The polymer was weighed, and the carbonate and cyclic content were then analyzed by ^1H NMR as described previously. These weights and NMR spectra were used to report the catalytic reactivity listed here after.

X-ray Structural Studies. A Bausch and Lomb 10× microscope was used to identify suitable crystals from a representative sample of crystals of the same habit. Crystals were coated with mineral oil, placed on a glass fiber, and mounted on a Bruker SMART 1000 CCD diffractometer. X-ray data were collected covering more than a hemisphere of reciprocal space by a combination of three sets of exposures. Each exposure had a different φ angle for the crystal orientation, and each exposure covered 0.3° in ω. The crystal to detector distance was 4.9 cm. Decay was monitored by repeating collection of the initial 50 frames collected and analyzing the duplicate reflections. Crystal decay was negligible. The space group was determined on the basis of systematic absences and intensity statistics.[13] The structure was solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed in idealized positions with fixed isotropic displacement parameters equal to 1.5 times (1.2 for methyl protons) the equivalent isotropic displacement parameters of the atom to which they are attached.

The following programs were used: data collection and cell refinement, SMART;[15] data reduction, SAINTPLUS(Bruker[16]); programs used to solve structures, SHELXS-97 (Sheldrick[17]); programs used to refine structures, SHELXL-99 (Sheldrick[18]); molecular graphics and publication materials, SHELXTL-Plus version 5.0 (Bruker[19]).

Results and Discussion

Previously we have developed an extensive library of salen ligands bearing electron-donating group for our investigations of chromium(III) salen derivatives as catalysts for the copolymerization of cyclohexene oxide and CO_2, for these were found to be most effective.[7,8] During the focus of this report we have established that more electron deficient salen ligands provide better aluminum(III) salen complexes which serve as catalysts for the epoxide/CO_2 coupling process (vide infra). Unfortunately, salen ligands containing electron-withdrawing substituents on the phenolate groups (e.g., chloride) are often insoluble in common organic solvents, in particular epoxides. To combat this we have synthesized two new salen ligands possessing both a solubilizing, electron-donating *tert*-butyl group at the 3-position of the phenolate ligand and an electron-withdrawing nitro group at the 5-position. These two ligands (^{t}Bu)(NO_2)salenH_2 (**1**) and (phen)(^{t}Bu)(NO_2)salenH_2 (**2**) were synthesized by following established procedures whereby 2 equiv of the appropriate salicylaldehyde are reacted with 1 equiv of an appropriate diamine in an alcohol solvent. Complete synthetic and spectroscopic details are presented in the Experimental Section. X-ray quality crystals of **1** were obtained from a concentrated dichloromethane solution by slow evaporation. A thermal ellipsoid representation is provided in Figure 1. Crystal and data collection parameters are listed in Table 1.

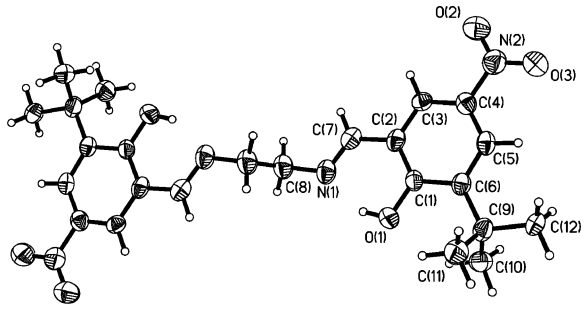

Figure 1. Thermal ellipsoid plot of **1**. Ellipsoids are at the 50% level.

Synthesis and Structures of Aluminum Salen Complexes. The direct reaction of salenH_2 with Et_2AlZ (Z = Et or Cl) proceeds rapidly with evolution of 2 equiv of ethane to give the target (salen)AlZ complexes in good yield as indicated in Scheme 1. It is important to note that the reaction may be readily conducted in toluene when the salen diimine is aliphatic but requires acetonitrile as the reaction solvent when the salen diimine is aromatic. When Z = Et, the axial ligand can be replaced by direct exchange with a phenol yielding **13** and **14**.

X-ray quality crystals of **4**, **7**, **13**, and **14** were obtained. The solid-state structures show that all four display the distorted square pyramidal geometry typical of group 13 salen complexes.[11,12,20−24] Crystal and data collection parameters are given in Table 1. Crystals of **4**·CH_2Cl_2 were obtained by slow evaporation of a concentrated CH_2Cl_2 solution at 10 °C. **4**·CH_2Cl_2 crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules and a molecule of CH_2Cl_2 in the asymmetric unit. A thermal ellipsoid plot is provided in Figure 2. Crystals of **7** were obtained by slow evaporation of a concentrated CH_2Cl_2 solution at 10 °C. **7** crystallizes in the monoclinic space group $P2_1/c$. The two carbons of the cyclohexyldiimine bound to the nitrogen atoms are disordered with the major orientation at 52% occupancy. A thermal ellipsoid plot is provided in Figure 3. Selected bond lengths and angles of **4** and **7** are

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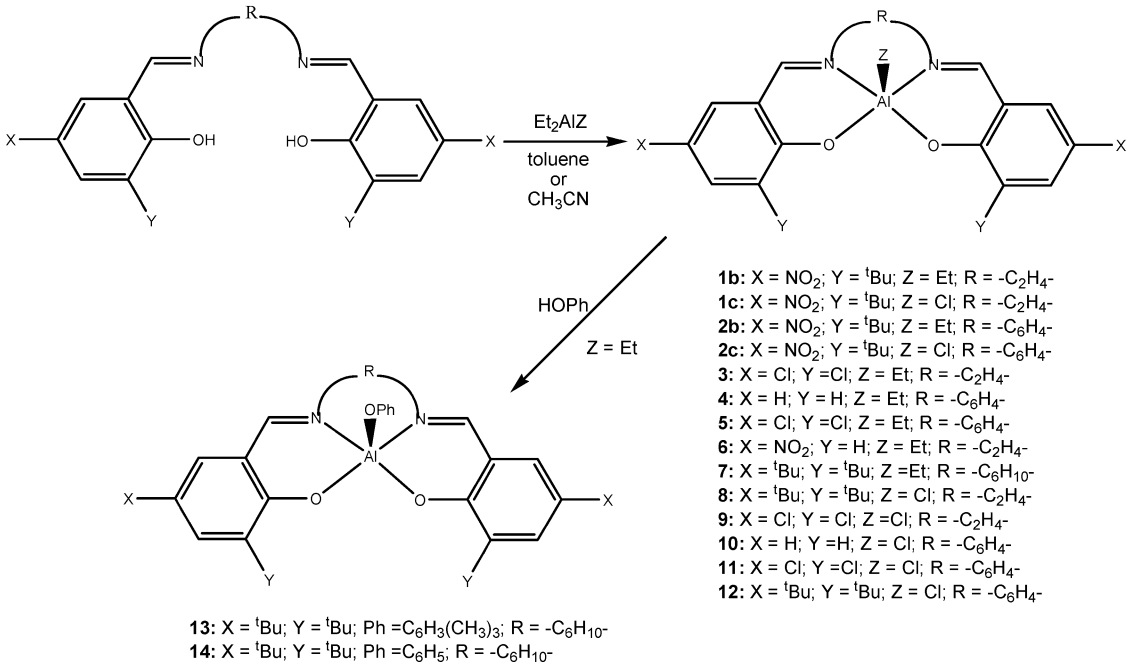
Table 1. Crystal Data and Structure Refinement

	1	**4**·CH_2Cl_2	**7**	**13**	**14**
empirical formula	$C_{18}H_{22.50}N_3O_{4.50}$	$C_{22}H_{18}AlN_2O_2 \cdot CH_2Cl_2$	$C_{38}H_{55}AlN_2O_2$	$C_{41}H_{57}AlN_2O_3$	$C_{38}H_{51}AlN_2O_3$
fw	352.89	454.3	598.82	652.87	610.79
temp (K)	110(2)	110(2)	110(2)	110(2)	110(2)
cryst system	rhombohedral	monoclinic	monoclinic	triclinic	triclinic
space group	$R\bar{3}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	24.557(4)	15.977(4)	17.223(5)	10.004(9)	11.608(6)
b (Å)	24.557(4)	28.209(7)	10.372(3)	14.185(12)	11.909(6)
c (Å)	10.193(2)	9.176(2)	19.645(6)	15.389(13)	15.176(7)
α (deg)	90	90	90	115.006(14)	111.451(10)
β (deg)	90	106.069(5)	99.558(7)	96.996(16)	109.693(9)
γ (deg)	120	90	90	96.653(17)	95.296(9)
V (Å^3)	5323.7(17)	3974.1(16)	3460.4(17)	1930(3)	1781.9(15)
D_c (Mg/m^3)	1.321	1.380	1.149	1.123	1.138
Z	12	4	4	2	2
μ (mm^{-1})	0.096	0.258	0.093	0.090	0.094
reflcns collcd	10 985	24 045	20 643	8953	11 761
indpndt reflcns	2696	8791	7732	5491	7713
params	158	516	400	439	409
goodness-of-fit on F^2	0.772	1.015	1.129	1.013	1.018
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1012$	$R_1 = 0.0865$	$R_1 = 0.0990$	$R_1 = 0.0513$	$R_1 = 0.0531$
	$R_w = 0.2186$	$R_w = 0.1908$	$R_w = 0.2215$	$R_w = 0.1195$	$R_w = 0.1212$
final R indices (all data)	$R_1 = 0.2232$	$R_1 = 0.1658$	$R_1 = 0.2713$	$R_1 = 0.0750$	$R_1 = 0.0904$
	$R_w = 0.2670$	$R_w = 0.2331$	$R_w = 0.2851$	$R_w = 0.1314$	$R_w = 0.1522$

Scheme 1



found in Tables 2 and 3. Despite the differences in electronics provided by the salen ligands of these two complexes, there are remarkable similarities in their geometries. The Al−C bond lengths of the axial ethyl groups are in close agreement (1.968(5) Å vs 1.960(9) Å), and the coordination sphere of the salen ligands are nearly identical. Both complexes are in concurrence with other published (salen)Al(alkyl) structures in terms of bond lengths and angles.[11,12]

Crystals of **13** and **14** were obtained by slow diffusion of pentane into a concentrated THF solution at −30 °C. **13** and **14** crystallize in the triclinic space group $P\bar{1}$. As would be expected, the geometries of these two complexes are very nearly identical with the greatest deviation belonging to the Al1−O2 bond length (1.792(2) Å vs 1.7717(17) Å). Thermal ellipsoid plots are provided in Figures 4 and 5. Bond lengths and angles in **13** are in agreement with those of {*N*,*N*′-bis(salicylidene)diethylimine}aluminum(III) 2,4,6-trimethylphenoxide previously published and are given in Tables 4 and 5.[20]

It is interesting to note that when Z = Et, as in **4** and **7**, the basal plane formed from N1, N2, O1, and O2 is quite planar with the rms deviation from planarity of the atoms equal to 0.0669(16) and 0.0736(16) Å for the two independent molecules of **4** and 0.0696(34) Å for **7**. The Al atom sits an average of 0.551(7) Å above the plane in the two molecules of **4** and 0.5484(41) Å in **7**. When Z = phenoxide, as in **13** and **14**, the same plane is more distorted. The rms deviation for **13** = 0.2321(10) Å, but the Al atom is located 0.4915(13) Å from the plane and the corresponding measurements are 0.2211(10) and 0.4626(10) Å for **14**.

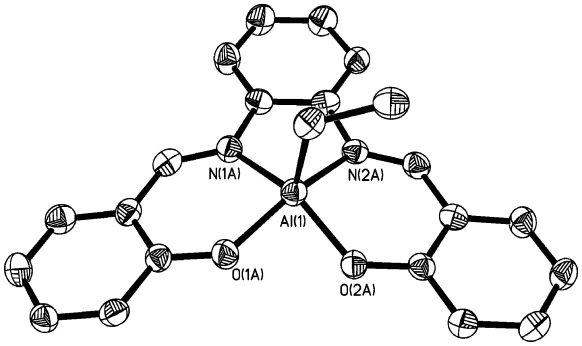


Figure 2. Thermal ellipsoid plot of **4**·CH_2Cl_2. Ellipsoids are at the 50% probability level. H atoms and one solvent molecule are omitted for clarity.

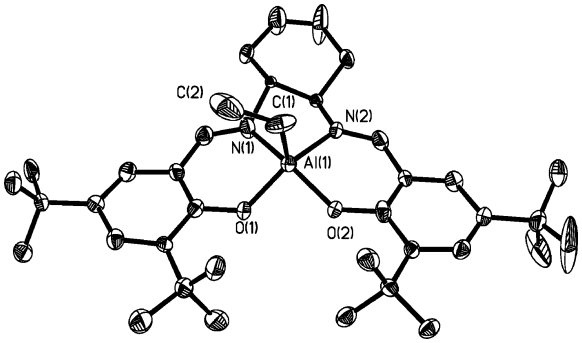


Figure 3. Thermal ellipsoid plot of **7**. Ellipsoids are at the 50% level. Only the major orientation of the disordered carbons adjacent to N1 and N2 is shown. H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) for **4**·CH_2Cl_2 and **7**

Al(1)−O(1A)	1.818(3)	Al(2)−O(1B)	1.808(3)
Al(1)−O(2A)	1.814(3)	Al(2)−O(2B)	1.823(3)
Al(1)−N(1A)	2.026(4)	Al(2)−N(1B)	2.051(4)
Al(1)−N(2A)	2.036(4)	Al(2)−N(2B)	2.014(4)
Al(1)−C(21A)	1.965(5)	Al(2)−C(21B)	1.968(5)
Al(1)−O(1)	1.799(6)	Al(1)−N(2)	2.015(7)
Al(1)−O(2)	1.816(5)	Al(1)−C(1)	1.960(9)
Al(1)−N(1)	2.046(7)		

Table 3. Selected Bond Angles (deg) for **4**·CH_2Cl_2 and **7**

O(2A)−Al(1)−O(1A)	86.80(14)	O(2B)−Al(2)−O(1B)	88.44(14)
O(2A)−Al(1)−C(21A)	110.35(17)	O(2B)−Al(2)−C(21B)	113.69(19)
O(1A)−Al(1)−C(21A)	109.25(18)	O(1B)−Al(2)−C(21B)	107.18(18)
O(2A)−Al(1)−N(1A)	141.75(15)	O(2B)−Al(2)−N(1B)	141.24(16)
O(1A)−Al(1)−N(1A)	88.56(14)	O(1B)−Al(2)−N(1B)	87.98(14)
C(21A)−Al(1)−N(1A)	107.01(17)	C(21B)−Al(2)−N(1B)	104.21(18)
O(2A)−Al(1)−N(2A)	88.03(14)	O(2B)−Al(2)−N(2B)	87.47(14)
O(1A)−Al(1)−N(2A)	151.03(15)	O(1B)−Al(2)−N(2B)	149.97(16)
C(21A)−Al(1)−N(2A)	99.27(17)	C(21B)−Al(2)−N(2B)	101.69(17)
N(1A)−Al(1)−N(2A)	78.12 (15)	N(1B)−Al(2)−N(2B)	76.95 (14)
O(2)−Al(1)−O(1)	89.6(2)	C(1)−Al(1)−N(1)	101.8(3)
O(2)−Al(1)−C(1)	106.8(3)	O(2)−Al(1)−N(2)	87.9(3)
O(1)−Al(1)−C(1)	110.6(4)	O(1)−Al(1)−N(2)	141.6(3)
O(2)−Al(1)−N(1)	150.6(3)	C(1)−Al(1)−N(2)	106.8(4)
O(1)−Al(1)−N(1)	86.5(3)	N(1)−Al(1)−N(2)	77.5(3)

Thus far, all other published (salen)AlZ structures possess the square pyramidal geometry displayed by the complexes reported herein. Nevertheless, it is possible that complexes such as complex **10** which contains a salen ligand devoid of substituents in the 3- and 5-positions of the phenolate rings might be dimeric, containing chloride bridging groups between the two metal centers.[23] Unfortunately, we were unable to obtain suitable crystals of **10** for characterization by X-ray analysis.

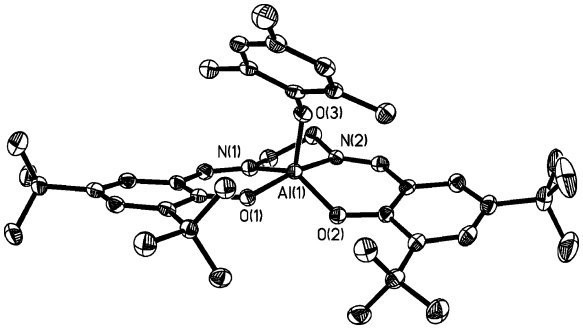


Figure 4. Thermal ellipsoid of **13**. Ellipsoids are at the 50% level. H atoms are omitted for clarity.

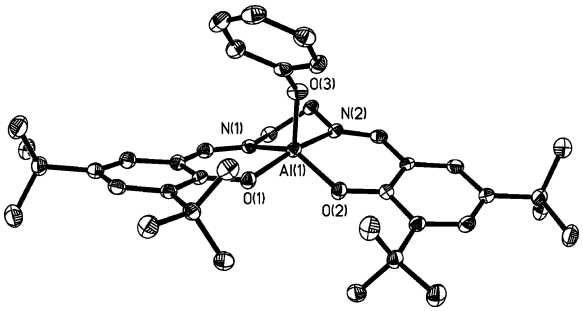


Figure 5. Thermal ellipsoid of **14**. Ellipsoids are at the 50% level. H atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) for **13** and **14**

13		14	
Al(1)−O(1)	1.800(2)	Al(1)−O(1)	1.8014(17)
Al(1)−O(2)	1.792(2)	Al(1)−O(2)	1.7717(17)
Al(1)−O(3)	1.750(2)	Al(1)−O(3)	1.7476(17)
Al(1)−N(1)	1.986(3)	Al(1)−N(1)	1.985(2)
Al(1)−N(2)	2.001(2)	Al(1)−N(2)	1.9931(19)

Table 5. Selected Bond Angles (deg) for **13** and **14**

13		14	
O(3)−Al(1)−O(2)	114.85(9)	O(3)−Al(1)−O(2)	114.59(8)
O(3)−Al(1)−O(1)	103.83(10)	O(3)−Al(1)−O(1)	103.79(8)
O(2)−Al(1)−O1)	91.73(10)	O(2)−Al(1)−O(1)	90.83(8)
O(3)−Al(1)−N(1)	109.33(9)	O(3)−Al(1)−N(1)	107.33(8)
O(2)−Al(1)−N(1)	134.14(10)	O(2)−Al(1)−N(1)	136.71(8)
O(1)−Al(1)−N(1)	89.20(10)	O(1)−Al(1)−N(1)	89.33(8)
O(3)−Al(1)−N(2)	91.74(10)	O(3)−Al(1)−N(2)	90.63(8)
O(2)−Al(1)−N(2)	88.01(11)	O(2)−Al(1)−N(2)	89.24(8)
O(1)−Al(1)−N(2)	162.89(9)	O(1)−Al(1)−N(2)	164.06(8)
N(1)−Al(1)−N(2)	78.84(11)	N(1)−Al(1)−N(2)	79.77(8)

Copolymerization of Cyclohexene Oxide and Carbon Dioxide. Our initial studies utilizing aluminum salen derivatives as potential catalysts for the coupling of cyclohexene oxide and CO_2 focused on salen ligand frameworks similar to those found in our most active chromium catalysts for this process.[7] That is, we investigated complexes processing electron-donating *tert*-butyl substituents in the 3- and 5-positions of the phenolate rings, **7** and **8**, paired with the most effective Lewis base cocatalysts (phosphines or PPNX salts). The experiments involving phosphines (PPh_3 or PCy_3) as cocatalysts for the copolymerization reaction proved to be unsuccessful, producing low molecular weights oligomers with ether linkages in excess of 50% and large amounts of cyclic carbonate. Reactions carried out in the presence of a

[PPN][Cl] cocatalyst produced only cyclic carbonate. In an attempt to increase the reactivity of these complexes, the axial ligand was changed to a phenoxide, complexes **13** and **14**. Nevertheless, these alterations did little to enhance the reactivity of these complexes, producing copolymer detectable by infrared spectroscopy but not in isolable quantities (<0.15 g).

Recent studies by Gibson and co-workers have indicated that increasing the electrophilicity of the metal center by adding electron-withdrawing groups to the phenolate rings of the salen ligands increases the complexes' ability to catalyze the polymerization of (D,L)- and (L)-lactide at ambient temperatures.[21] We have employed a similar strategy by removing the *tert*-butyl groups from the phenolate ring, utilizing complexes **4** and **10**. Employing **4** as a catalyst with PPNCl provided poly(cyclohexene carbonate) in good yield but with a sizable quantity of cyclic carbonate. However, attempts at using complex **10** with PPNCl as a cocatalyst proved ineffective due to their insolubility in a common organic solvent.[25] In addition, efforts to increase the electrophilicity of the metal center by employing highly electron withdrawing chloro groups at the 3- and 5-positions of the phenolate rings were accomplished with the synthesis of complexes **3** and **11**. However, to obtain highly soluble electron-deficient metal salen complexes it was necessary to introduce solubilizing electron-donating *tert*-butyl groups in the 3-positions offset with strongly electron-withdrawing nitro groups in the 5-position. Using these salen ligands, complexes **1b**,**c** and **2b**,**c** were prepared.

On the basis of previous studies which have shown that aluminum porphyrinates and aluminum salen derivatives produce polycarbonates and cyclic carbonates,[1c,26] respectively, in the presence of tetrabutylammonium salts ($Bu_4N^+X^-$), we have examined these salts as cocatalysts in conjunction with our aluminum salen complexes for their ability to copolymerize cyclohexene oxide and carbon dioxide. These salts have the benefits over their PPN^+ analogues of being relatively inexpensive and readily soluble in epoxide. For example, the combination of any of our aluminum salen complexes with a Bu_4N^+ salt produced a complex soluble in cyclohexene oxide. We have conducted copolymerization studies with **1b**,**c**, **3**, **4**, **9**, and **10** in combination with $Bu_4N^+X^-$ (X = N_3, Cl, or OAc). Results of these copolymerization studies are summarized in Table 6.

These studies show that, in almost all cases, the (salen)AlCl complexes are more active than their (salen)AlEt counterparts as displayed by the turnover frequency (TOF). The most active catalyst/cocatalyst combination, (^{t}Bu)(NO_2)salenAlCl and Bu_4NCl (Table 6, entry 4), has a TOF = 35.4 mol of epoxide consumed/(mol of Al·h). The worst among the active species, (phen)salenAlEt and Bu_4NCl (Table 6, entry 11), has a TOF = 5.2 mol of epoxide consumed/(mol of Al·h). However, we could not establish any trends for the series of catalysts or cocatalysts. For example, while **4** follows the trend $Cl^- < N_3^- < OAc^-$ in terms of increasing reactivity, **1c** follows the trend $N_3^- < OAc^- < Cl^-$. Nevertheless, there were not major differences in the activities of these aluminum salen complexes with variation in these Bu_4N^+ salts. The catalysts were however very susceptible to changes in the electronic character of the salen ligand. For example, the modification from (^{t}Bu)(NO_2)-salenAlEt (**1b**) to (NO_2)salenAlEt (**6**) produced an inactive species in combination with Bu_4N^+ salts as cocatalysts. Alteration of the diimine backbone can also drastically effect catalytic activity. That is, active catalyst/cocatalyst combinations, (^{t}Bu)(NO_2)salenAlEt/Bu_4NN_3 (Table 6, entry 2) and {(Cl)$_2$salen}AlEt/Bu_4NN_3 (Table 6, entry 9), become completely inactive by changing the diimine backbone from ethylenediamine to 1,2-phenylenediamine. Likewise, a change from {(^{t}Bu)$_2$salen}AlCl (**8**) to {(phen)-(^{t}Bu)$_2$salen}AlCl (**12**) produces an active species in conjunction with Bu_4NN_3. This particular combination produces a large amount of cyclic carbonate in addition to the copolymer, but it is interesting to note the significant increase in activity over that of complex **8** under similar reaction conditions.

Table 6. Copolymerization of Cyclohexene Oxide and Carbon Dioxide[a]

run	catal[b]	cocatal[b]	TOF[c]	% cyclic[d]	% CO_2[d]
1	1b	Bu_4NCl	15.0	4	98
2	1b	Bu_4NN_3	20.7	2	95
3	1b	Bu_4NOAc	28.2	1	98
4	1c	Bu_4NCl	35.4	3	96
5	1c	Bu_4NN_3	27.2	<1	>99
6	1c	Bu_4NOAc	25.8	2	98
7	1c	None	24.2	10	74
8	3	Bu_4NCl	20.6	5	98
9	3	Bu_4NN_3	7.3	2	96
10	3	Bu_4NOAc	26.0	3	97
11	4	Bu_4NCl	5.2	4	90
12	4	Bu_4NN_3	15.3	1	93
13	4	Bu_4NOAc	17.7	3	95
14	9	Bu_4NCl	23.2	5	94
15	9	Bu_4NN_3	18.0	4	97
16	9	Bu_4NOAc	12.7	7	92
17	10	Bu_4NCl	11.5	3	99
18	10	Bu_4NN_3	23.3	4	99
19	10	Bu_4NOAc	28.7	2	99

[a] 500 psi of CO_2 at 80 °C. [b] 50 mg of catalyst and 1 equiv of cocatalyst. [c] mol of epoxide consumed/(mol of Al·h) based on 8 h reaction times. [d] Estimated via ^{1}H NMR.

Since the TOF listed in Table 6 were determined from isolated yields, in situ infrared monitoring of one catalyst system, specifically complex **1c** with the various $Bu_4N^+X^-$ cocatalysts, was performed for comparative purposes. Figure 6 displays the time traces of the absorbances due to the ν_{CO_2} vibrational mode of the copolymer at 1750 cm^{-1} for these processes. As can be seen from a comparison of the data in Table 6 with Figure 6, there is little difference noted for the three binary catalyst systems studied, with the **1c**/$Bu_4N^+Cl^-$ combination being the most effective. Fur-

(25) It is necessary to first stir the solubilized metal salen complexes and PPNCl salt in a common organic solvent (typically CH_2Cl_2 or benzene/methanol), thereby forming the six-coordinate anionic complex which is soluble in the epoxide. The thus formed metal derivative is dried under vacuum prior to its use as a catalyst.

(26) (a) Lu, X.-B.; Feng, X.-J.; He, R. *Appl. Catal., A* **2002**, *234*, 25. (b) Lu, X.-B.; Zhang, Y.; Bin, L.; Hui, W.; He, R. *Chin. J. Catal.* **2003**, *24*, 317. (c) Lu, X.-B.; Zhang, Y.; Liang, B.; Li, X.; Wang, H. *J. Mol. Catal., A* **2004**, *210*, 31. (d) Lu, X.-B.; Zhang, Y.-J.; Jin, K.; Luo, L.-M.; Wang, H. *J. Catal.* **2004**, *227*, 537−541.

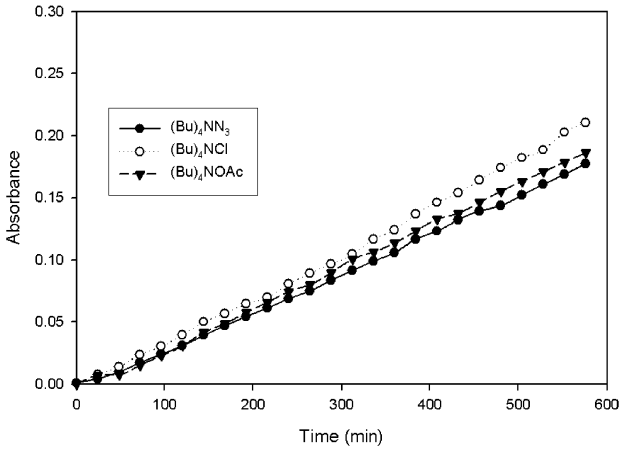


Figure 6. Peak profiles of the carbonate signal at 1750 cm^{-1} for in situ infrared monitoring of the copolymerization reactions involving **1c** and three tetrabutylammonium salts.

Table 7. Copolymerization of Cyclohexene Oxide and Carbon Dioxide[a]

run	catal	cocatal[b]	TOF[c]	% cyclic[d]	% CO_2[d]
1	1c	*N*-MeIm (1)	14.9	6	81
2	1c	*N*-MeIm (2.5)	17.0	3	93
3	1c	DMAP (1)	27.7	2	97
4	1c	DMAP (3)	32.0	2	96
5	1c	pyridine (1)	7.6	6	61
6	1b	DMAP (1)	18.0	4	90
7	10	*N*-MeIm (2.5)	7.2	4	92
8	10	DMAP (1)	14.9	3	91
9	10	pyridine (2.5)	2.5	5	85
10	4	*N*-MeIm[e]	1.9	34	48

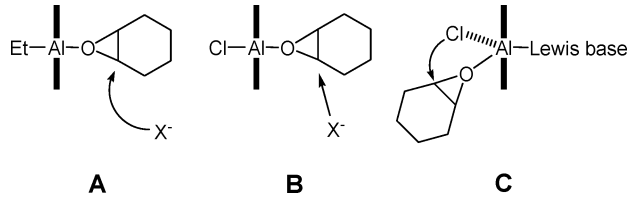
[a] 500 psi of CO_2 at 80 °C. [b] Equivalents of cocatalyst show in parentheses. [c] mol of epoxide consumed/(mol of Al·h) based on 8 h reaction times. [d] Estimated via ^1H NMR. [e] In the presence of 1 equiv of methanol.

thermore, it is of importance to note that the (salen)AlCl catalyst (**1c**) in the absence of a $Bu_4N^+X^-$ cocatalyst affords a copolymer with a substantial reduction in CO_2 content along with a significant rise in cyclic carbonate production.

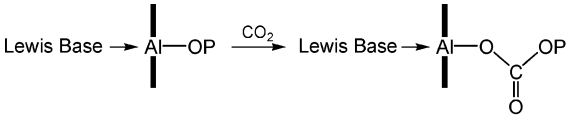
As mentioned earlier, there are several reports of aluminum porphyrin derivatives employed as catalysts in conjunction with the Lewis base cocatalysts, 1-methylimidazole (*N*-MeIm) and 4-(dimethylamino)pyridine (DMAP), for the copolymerization of epoxides and carbon dioxide.[1,4] Similarly, we and others have carried out extensive studies of this process utilizing a wide variety of (salen)CrX catalysts in the presence of *N*-MeIm and DMAP.[5,7] Hence, we have examined herein the activity of our more effective (salen)AlZ catalysts in the presence of the neutral Lewis bases *N*-MeIm, DMAP, and pyridine. The results of these studies are summarized in Table 7.

It is evident from the results reported in Table 7 that for both complex **1c** and **10** the order of activity as a function of cocatalyst is DMAP > *N*-MeIm > pyridine. Furthermore, as has been observed in the (salen)CrX-catalyzed system, complex **1c** in the presence of 1 equiv of *N*-MeIm results in a lower TOF as well as a reduction in carbonate linkages in the copolymer than in the presence of 3 equiv of *N*-MeIm. A similar less dramatic increase in TOF is seen for **1c** in the presence of 3 equiv of the more strongly

Scheme 2



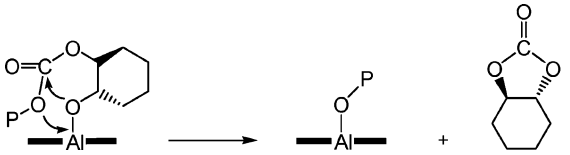
interacting DMAP cocatalyst vs 1 equiv. The increase in the CO_2 content noted in the copolymer afforded upon increasing the relative concentration of *N*-MeIm to **1c** (run 2 vs run 1 in Table 7) is consistent with the CO_2 insertion process being greatly accelerated in the presence of a good donating ligand trans to the growing polymer chain (see eq 2). A similar explanation accounts for the lower percentage of carbonate linkages in the copolymer produced utilizing the poorer donating Lewis base, pyridine as cocatalyst (runs 5 and 9 in Tables 7). These observations are in complete agreement with the proposed mechanism, supported by experimental data, described by Chisholm and Zhou for the (TPP)AlX (TPP = tetraphenylporphyrin) catalyzed coupling of propylene oxide and CO_2 in the presence of DMAP.[4]



(2)

P = growing polymer chain

Concomitantly, in the absence of a strong coordinating Lewis base cocatalyst the active five-coordinate aluminum species containing the growing polymer chain exists as the alkoxide intermediate for an extended period of time, thereby allowing for production of the cyclic carbonate via the backbiting mechanism as depicted in eq 3.



(3)

The most striking example of this can be seen in run 7 of Table 6 for the (salen)AlCl catalyst (**1c**) in the absence of a cocatalyst. Similar trends in product selectivity are noted for the (salen)CrCl-catalyzed coupling of cyclohexene oxide or propylene oxide and CO_2 as the carbon dioxide pressure is reduced.[5c,27] Finally, an attempt to activate the potentially most active (salen)AlEt derivative (complex **4**) with 1 equiv of methanol in the presence of the cocatalyst *N*-MeIm was unsuccessful (run 10 in Table 7).[28] Consistent with the detailed mechanistic studies of Chisholm and Zhou[4] for the (TPP)AlX/DMAP system, we propose the initiation steps to

(27) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2004**, in press.

(28) Consistent with the lack of activity of complex **4** under these circumstances it was found via ^1H NMR to be unchanged after extended reaction time in refluxing methanol. By way of contrast, the aluminum salen derivative containing an electron-donating salen ligand, complex **7**, easily underwent alcoholysis at ambient temperature.

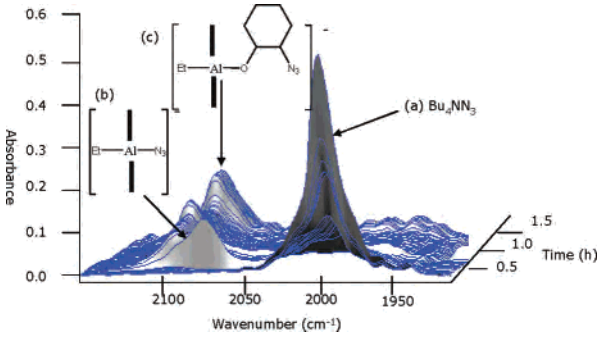


Figure 7. IR stack plot showing ring-opening of epoxide by (salen)AlEt and Bu_4NN_3 in three steps. (a) Bu_4NN_3 is added to reactor at 80 °C in 13 mL of toluene giving $\nu_{N_3} = 1999$ cm^{-1}. (b) At $t = 24$ min, 1 equiv of (salen)AlEt is added in 5 mL of toluene with an immediate decrease of signal at 1999 cm^{-1} and ν_{N_3} shifts to 2073 cm^{-1} indicating formation of six-coordinate aluminum species. (c) At $t = 81$ min, 276 equiv (5 mL) of cyclohexene oxide is added and ν_{N_3} shifts to 2095 cm^{-1} indicating formation of ring-opened epoxide product. At $t =$ 180 min the reactor was charged with 200 psi of CO_2 and growth of signal at 1750 cm^{-1} was observed indicating insertion of CO_2 and copolymer formation.

proceed via the epoxide ring-opening processes depicted in Scheme 2. In situ infrared spectra of the ring-opening process described in **A** involving a (salen)AlEt catalyst in the presence of the Bu_4NN_3 cocatalyst are contained in Figure 7. The process described in run 10 of Table 7 would be initiated via a species analogue to **C**, where chloride would be replaced by methoxide. It is important to recall here that the ring-opening of epoxides catalyzed by aluminum tetraphenylporphyrin complexes has been shown to be first-order in [Al].[4] This observation is consistent with the fact that when utilizing chiral aluminum salen derivatives as catalysts, this ring-opening process occurs with high % conversion but low % ee. On the other hand, the chiral chromium salen analogue complexes, which have been shown to ring open epoxides via a process second-order in [Cr], proceeds with both high activity as well as high % ee.[29]

Concluding Remarks

We have synthesized and characterized an array of five-coordinate aluminum salen complexes with various perturbations of the salen ligand via modifications at the 3- and 5-positions of the phenolate ring as well as the diimine backbone. These aluminum derivatives were employed as catalysts in conjunction with a series of anionic and neutral cocatalysts to affect the copolymerization of carbon dioxide and cyclohexene oxide. Our studies have shown that, in general, a more electron-withdrawing salen framework is necessary to produce significant quantities of copolymer with a high CO_2 content and an absence of the concurrent synthesis of sizable quantities of cyclic carbonate. In all variations of salen ligand, apical group, and cocatalyst, the aluminum salen catalysts are considerably less active than our previously described chromium salen systems; that is, the TOF obtained in this instance ranges from 5.2 to 35.4 h^{-1}, while chromium systems under similar conditions possess TOF's as high as 1150 h^{-1}. Despite their lower activities for the coupling of CO_2 and epoxides these aluminum salen complexes aid in supporting some of our earlier mechanistic proposals put forth for the chromium salen derivatives. For example, an increase in the concentration and/or donating ability of the neutral Lewis base cocatalysts, *or species derived therefrom*, enhances both TOF and CO_2 incorporation.

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Supporting Information Available: Complete details for the crystallographic studies of complexes **1**, **4**·CH_2Cl, **7**, **13**, and **14** in CIF format. This material is available free of change via the Internet at http://pubs.acs.org.

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