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Dinuclear Aluminum Complexes as Catalysts for Cycloaddition of CO_2 to Epoxides

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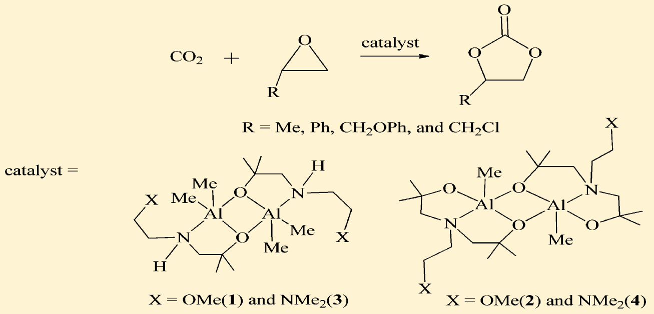
Ⓢ *Supporting Information*



ABSTRACT: The synthesis and characterization of dinuclear aluminum complexes bearing multidentate aliphatic aminoethanol-based ligands are presented. Single-crystal X-ray analyses, NMR data, and mass data reveal that four aluminum complexes synthesized are all dimeric in the solid, solution, and gas states. Especially, ^{27}Al NMR spectra have demonstrated that they exist as both five-coordinate Al(III) species in benzene-d_6 solution. All aluminum complexes are effective catalysts for the cycloaddition of CO_2 to propylene oxide in the presence of n-Bu_4NI as a cocatalyst. Complexes **1** and **3**, which have two methyl groups per aluminum center, are better catalytic systems than the corresponding complexes **2** and **4** with a mono methyl group per aluminum. In addition, complexes **3** and **4** containing a pendant $-CH_2CH_2NMe_2$ group attached to nitrogen showed the higher activity than those **1** and **2** with a pendant $-CH_2CH_2OMe$ group did. As expected, the catalytic activity for **3** increases as the reaction temperature increases up to 130 °C. In addition, compound **3** showed the highest activity for the cycloaddition of CO_2 with propylene oxide in the presence of tetrabutylphosphonium bromide as a cocatalyst.

■ INTRODUCTION

Cyclic carbonates could be prepared from the cycloaddition of CO_2 to epoxides, and they are proving to be valuable, for example, as aprotic solvents,[1] electrolytes for secondary batteries,[2] and starting materials for polycarbonates,[3] pharmaceutical intermediates,[4] enantiopure aminoalcohols,[5] and thermosetting coatings.[6]

The synthesis of cyclic carbonates from CO_2 and epoxides with metal catalysts and nonmetal organocatalysts has been intensively studied over the past few decades.[7] Many types of metal complexes (e.g., of aluminum,[8] chromium,[9] cobalt,[10] copper,[11] germanium,[12] indium,[13] nickel,[14] palladium,[15] rhenium,[16] ruthenium,[17] tin,[18] titanium,[19] and zinc[20] metal complexes) and nonmetal organocatalysts[21] have been found to be active catalytic systems for the synthesis of cyclic carbonates.

Many examples of aluminum compounds as catalysts for the cycloaddition reaction of CO_2 to epoxides have been reported in the literature.[8,22−26] Until now, much of the research focused on aluminum catalysts for the synthesis of cyclic carbonate has been directed toward the modification of aromatic chelating ligands, such as tetradentate salen-based ligands,[8,22,23] tetradentate tris(phenolate)amine ligands,[24] tetradentate porphyrin-based ligands,[25] and bidentate phenolic ligands.[26] To our best knowledge, dimeric aluminum catalysts chelated by aliphatic alkoxide ligands have never been used as catalysts for cyclic carbonate.

As shown in Scheme 1, we chose new aliphatic aminoethanol ligands with a pendant $-CH_2CH_2OMe$ or $-CH_2CH_2NMe_2$ group attached to nitrogen. Herein, we report the synthesis and characterization of aluminum complexes containing the novel multidentate aliphatic aminoethanol-based ligands and their use as catalysts for cycloaddition reaction of CO_2 to epoxides.

■ EXPERIMENTAL SECTION

General Considerations. All reactions of air- and moisture-sensitive materials were carried out under dinitrogen using standard Schlenk-type glassware on a dual manifold Schlenk line in a glovebox.[27] Dinitrogen was deoxygenated using activated Cu catalyst and dried with drierite.[28] All chemicals were purchased from Aldrich and used as supplied unless otherwise indicated. All solvents, toluene, diethyl ether, and n-hexane, were dried by distillation from sodium diphenylketyl under dinitrogen and were stored over 3 Å activated molecular sieves. $CDCl_3$ was dried over 4 Å activated molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve.

Measurements. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature on a 300 MHz NMR spectrometer using

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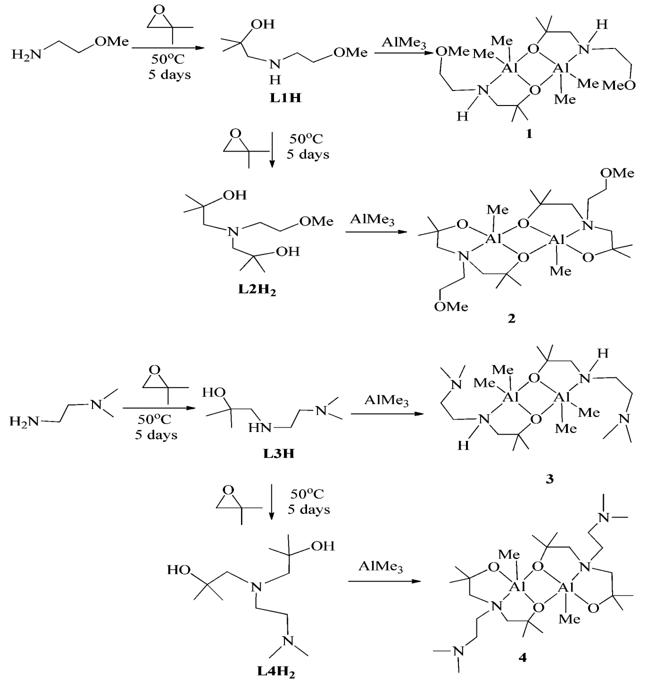
Scheme 1. Synthetic Routes for Al Complexes 1−4



standard parameters. All chemical shifts are reported in δ units with reference to the peaks of residual $CDCl_3$ (δ 7.24, ^{1}H NMR; δ 77.0, ^{13}CNMR) or C_6D_6 (δ 7.15, ^{1}H NMR; δ 128.0, ^{13}C NMR). ^{27}Al NMR spectra were obtained from Korea Basic Science Institute. Elemental analyses and mass data measurements were performed with an EA 1110-FISONS analyzer and VG Auto Spec., respectively.

Synthesis of $\mathrm{MeOCH_2CH_2NHCH_2CMe_2OH}$ (L1H). Isobutylene oxide (7.21 g, 100.0 mmol) and 2-methoxyethylamine (3.76 g, 50.0 mmol) were added to a 10 mL screw cap vial containing a stirring bar. The vial was tightly sealed with Teflon tape and paraffin film. The mixture was maintained at room temperature for overnight and was then heated for 5 days at 50 °C. The removal of volatile compounds at reduced pressure and distillation at 220−230 °C gave the desired product **L1H** (7.33 g, 67%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 3.45 (t, 2H, J = 5.09 Hz, $-\mathrm{OC}H_2\mathrm{CH_2N}-$), 3.33 (s, 3H, $-\mathrm{O}Me$), 2.80 (t, 2H, J = 5.09 Hz, $-\mathrm{OCH_2C}H_2\mathrm{N}-$), 2.51 (s, 2H, $-\mathrm{NC}H_2\mathrm{CMe_2}-$), 1.13 (s, 6H, $-\mathrm{NCH_2C}Me_2-$). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 72.0 ($-\mathrm{OCH_2CH_2N}-$), 69.1 ($-\mathrm{NCH_2CMe_2}-$), 60.1 ($-\mathrm{O}Me$), 58.8 ($-\mathrm{NC}H_2\mathrm{CH_2N}-$), 50.0 ($-\mathrm{NCH_2CMe_2}-$), 27.3 ($-\mathrm{NCH_2C}Me_2-$). EI-MS (% intensity): m/z 147 (6.49%, M^+), 132 (39.3%, $M^+ - CH_3$), 102 (46.4%, $M^+ - \mathrm{CH_2OMe}$), 88 (100%, $M^+ - \mathrm{CH_2CH_2OMe}$), 72 (33.1%, $M^+ - \mathrm{CH_2CH_2OMe} - \mathrm{OH}$), 57 (64.6%, $M^+ - \mathrm{Me} - \mathrm{CH_2CMe_2OH}$).

Synthesis of $\mathrm{MeOCH_2CH_2N(CH_2CMe_2OH)_2}$ ($\mathbf{L2H_2}$). $\mathbf{L2H_2}$ as a colorless oil was prepared by reacting isobutylene oxide (4.33 g, 60.0 mmol) with **L1H** (4.42 g, 30.0 mmol) in a manner analogous to the procedure for **L1H**. The removal of volatile compounds at reduced pressure and distillation at 280−290 °C gave the desired product $\mathbf{L2H_2}$ (4.83 g, 65.7%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 3.41 (t, 2H, J = 5.52 Hz, $-\mathrm{OC}H_2\mathrm{CH_2N}-$), 3.34 (s, 3H, $-\mathrm{O}Me$), 2.84 (t, 2H, J = 5.51 Hz, $-\mathrm{OCH_2C}H_2\mathrm{N}-$), 2.60 (s, 4H, $-\mathrm{NC}H_2\mathrm{CMe_2}-$), 1.16 (s, 12H, $-\mathrm{NCH_2C}Me_2-$). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 71.6 ($-\mathrm{OCH_2CH_2N}-$), 70.7 ($-\mathrm{NCH_2CMe_2}-$), 69.2 ($-\mathrm{O}Me$), 59.1 ($-\mathrm{OCH_2CH_2N}-$), 58.8 ($-\mathrm{NCH_2CMe_2}-$), 28.1 ($-\mathrm{NCH_2C}Me_2-$). EI-MS (% intensity): m/z 220 (8.31%, M^+), 204 (53.3%, $M^+ - CH_3$), 160 (51.6%, $M^+ - \mathrm{CH_2CH_2OMe}$), 102 (53.1%, $M^+ - \mathrm{CH_2CH_2OMe} - \mathrm{CMe_2OH}$), 88 (69.4%, $M^+ - \mathrm{CH_2CH_2OMe} - \mathrm{CH_2CMe_2OH}$), 59 (100%, $M^+ - \mathrm{N(CH_2CMe_2OH)_2}$).

Synthesis of $\mathrm{Me_2NCH_2CH_2NHCH_2CMe_2OH}$ (L3H). **L3H** as a colorless oil was prepared by reacting isobutylene oxide (7.93 g, 110.0 mmol) with *N,N*-dimethylethylenediamine (4.41 g, 50.0 mmol) in a manner analogous to the procedure for **L1H**. The removal of volatile compounds at reduced pressure and distillation at 240−250 °C gave the desired product **L3H** (6.47 g, 80.7%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 2.70 (t, 2H, J = 6.07 Hz, $-\mathrm{NC}H_2\mathrm{CH_2NMe_2}-$), 2.49 (s, 2H, $-\mathrm{NC}H_2\mathrm{CMe_2}-$), 2.35 (t, 2H, J = 6.06 Hz, $-\mathrm{NCH_2C}H_2\mathrm{NMe_2}-$), 2.18 (s, 6H, $-\mathrm{N}Me_2$), 1.12 (s, 6H, $-\mathrm{NCH_2C}Me_2-$). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 69.1 ($-\mathrm{NCH_2CMe_2}-$), 60.2 ($-\mathrm{NCH_2CH_2NMe_2}-$), 59.2 ($-\mathrm{NCH_2CH_2NMe_2}-$), 48.0 ($-\mathrm{NCH_2CMe_2}-$), 45.5 ($-\mathrm{N}Me_2$), 27.4 ($-\mathrm{NCH_2C}Me_2-$). EI-MS (% intensity): m/z 160 (38.9%, M^+), 116 (52.8%, $M^+ - \mathrm{NMe_2}$), 102 (61.4%, $M^+ - \mathrm{CH_2NMe_2}$), 85 (39.3%, $M^+ - \mathrm{CH_2NMe_2{-}OH}$), 71 (43.4%, $M^+ - \mathrm{CH_2CH_2NMe_2{-}OH}$), 59 (100%, $M^+ - \mathrm{HNCH_2(CH_2CH_2NMe_2)}$).

Synthesis of $\mathrm{Me_2NCH_2CH_2N(CH_2CMe_2OH)_2}$ ($\mathbf{L4H_2}$). $\mathbf{L4H_2}$ as a colorless oil was prepared by reacting isobutylene oxide (4.33 g, 60.0 mmol) with **L3H** (4.81 g, 30.0 mmol) in a manner analogous to the procedure for **L1H**. The removal of volatile compounds at reduced pressure and distillation at 290−300 °C gave the desired product $\mathbf{L4H_2}$ (3.99 g, 57.2%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 2.76 (t, 2H, J = 6.12 Hz, $-\mathrm{NC}H_2\mathrm{CH_2NMe_2}-$), 2.58 (s, 4H, $-\mathrm{NC}H_2\mathrm{CMe_2}-$), 2.38 (t, 2H, J = 6.11 Hz, $-\mathrm{NCH_2C}H_2\mathrm{NMe_2}-$), 2.21 (s, 6H, $-\mathrm{N}Me_2$), 1.16 (s, 12H, $-\mathrm{NCH_2C}Me_2$). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 70.5 ($-\mathrm{NCH_2CMe_2}-$), 69.5 ($-\mathrm{NCH_2CMe_2}-$), 58.9 ($-\mathrm{NCH_2CH_2NMe_2}-$), 57.1 ($-\mathrm{NCH_2CH_2NMe_2}-$), 45.6 ($-\mathrm{N}Me_2$), 28.4 ($-\mathrm{NCH_2C}Me_2-$). EI-MS (% intensity): m/z 233 (24.5%, M^+), 174 (53.7%, $M^+ - \mathrm{CH_2NMe_2}$), 173 (68.6%, $M^+ - \mathrm{CMe_2OH}$), 72 (99.7%, $M^+ - \mathrm{N(CH_2CMe_2OH)_2}$), 59 (96.3%, $M^+ - \mathrm{CH_2NCH_2CMe_2OH(CH_2CH_2NMe_2)}$), 58 (45.6%, $M^+ - \mathrm{CH_2N(CH_2CMe_2OH)_2}$).

Synthesis of $\mathrm{\{Me_2Al(OCMe_2CH_2)HNCH_2CH_2OMe\}_2}$ (1). To a stirred colorless solution of **L1H** (0.294 g, 2.0 mmol) in 30 mL of toluene was added $AlMe_3$ (1 mL of a 2.0 M solution in toluene, 2.0 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for overnight. The residue, obtained by removing the solvent under vacuum, was recrystallized in toluene. The desired product **1** was isolated as colorless crystals after the solution remained at −15 °C in a refrigerator for a few days (71.1%, 0.29 g). ^{1}H NMR (C_6D_6, 300.13 MHz): δ 3.10 (t, 4H, J = 4.94 Hz), 3.01 (s, 6H), 2.59−2.54 (m, 4H), 2.36 (t, 2H, J = 7.58 Hz), 2.09 (d, 4H, J = 8.79 Hz), 1.26 (s, 12H), −0.43 (s, 12H). ^{13}C NMR (C_6D_6, 75.46 MHz): δ 70.4, 69.2, 60.1, 58.3, 48.2, 27.7, −4.85. ^{27}Al NMR (C_6D_6, 104.26 MHz): δ 93.3 ($\Delta\nu_{1/2}$ = 2346 Hz). EI-MS (% intensity): m/z 406 (100%, M^+). Anal. Calcd. for $C_{18}H_{44}N_2O_4Al_2$: C, 53.18; H, 10.91; N, 6.89. Found: C, 52.98; H, 10.94; N, 6.72.

Synthesis of $\mathrm{\{MeAl(OCMe_2CH_2)_2NCH_2CH_2OMe\}_2}$ (2). In a manner analogous to the procedure for **1**, the desired product **2** was prepared from a toluene solution of $AlMe_3$ ((1 mL of 2.0 M solution in toluene, 2.0 mmol) and $\mathbf{L2H_2}$ (0.438 g, 2.0 mmol) in a yield of 79.1% (0.41 g). ^{1}H NMR (C_6C_6, 300.13 MHz): δ 3.05−2.96 (m, 8H), 2.96 (s, 6H), 2.91 (s, 2H), 2.69 (d, 2H, J = 12.7 Hz), 2.46 (d, 4H, J = 12.6 Hz), 1.61 (s, 6H), 1.42 (s, 6H), 1.39 (s, 6H), 1.33 (s, 6H), −0.32 (s, 6H). ^{13}C NMR (C_6D_6, 75.46 MHz): δ 71.5, 69.6, 69.0, 68.7, 68.0, 58.5, 58.0, 33.1, 32.5, 29.9, 29.6, −6.53. ^{27}Al NMR (C_6D_6, 104.26 MHz): δ 95.8 ($\Delta\nu_{1/2}$ = 2137 Hz). EI-MS (% intensity): m/z 518 (68%, M^+), 503 (100%, $M^+ - CH_3$). Anal. Calcd. for $C_{24}H_{52}N_2O_6Al_2$: C, 55.58; H, 10.11; N, 5.40. Found: C, 55.52; H, 10.50; N, 5.25.

Synthesis of $\mathrm{\{Me_2Al(OCMe_2CH_2NHCH_2CH_2NMe_2)\}_2}$ (3). In a manner analogous to the procedure for **1**, the desired product **3** was prepared from a toluene solution of $AlMe_3$ (1.25 mL of a 2.0 M solution in toluene, 2.5 mmol) and **L3H** (0.401 g, 2.5 mmol) in a yield of 88.4% (0.48 g). ^{1}H NMR (C_6D_6, 300.13 MHz): δ 2.76 (t, 2H, J = 6.29 Hz), 2.47 (d, 4H, J = 4.38 Hz), 2.15 (d, 4H, J = 8.76 Hz), 2.35 (t, 4H, J = 5.43 Hz), 1.94 (s, 12H), 1.35 (s, 12H), −0.4 (s, 12H). ^{13}C NMR (C_6D_6, 75.46 MHz): δ 70.4, 59.8, 56.1, 45.2, 45.1, 27.4, −4.74. ^{27}Al NMR (C_6D_6, 104.26 MHz): δ 94.5 ($\Delta\nu_{1/2}$ = 2971 Hz). EI-MS (% intensity): m/z 430 (100%, M^+). Anal. Calcd. for $C_{20}H_{50}N_4O_2Al_2$: C, 55.53; H, 11.65; N, 12.95. Found: C, 55.90; H, 12.02; N, 13.12.

Synthesis of $\mathrm{\{MeAl(OCMe_2CH_2)_2NCH_2CH_2NMe_2)\}_2}$ (4). In a manner analogous to the procedure for **1**, the desired product **4** was prepared from a toluene solution of $AlMe_3$ (1.5 mL of a 2.0 M solution in toluene, 3.0 mmol) and **L4H$_2$** (0.697 g, 3.0 mmol) in a yield of 69.3% (0.57 g). ^{1}H NMR (C_6D_6, 300.13 MHz): δ 3.06−3.00 (m, 4H), 2.83 (d, 2H, J = 13.5 Hz), 2.83 (d, 2H, J = 13.5 Hz), 2.39 (d, 2H, J = 12.6 Hz), 2.36 (t, 2H, J = 13.6 Hz), 2.27 (t, 2H, J = 6.69 Hz), 2.19−2.11(m, 2H), 1.98 (s, 12H), 1.62 (s, 6H), 1.43 (s, 6H), 1.39 (s, 6H), 1.35 (s, 6H), −0.29 (s, 6H). ^{13}C NMR (C_6D_6, 75.46 MHz): δ 71.4, 69.6, 69.1, 67.1, 56.6, 54.2, 45.7, 33.0, 32.4, 29.9, 29.5, −6.37. ^{27}Al NMR (C_6D_6, 104.26 MHz): δ 98.6 ($\Delta\nu_{1/2}$ = 2450 Hz). EI-MS (% intensity): m/z 544 (55%, M$^+$), 529 (100%, M$^+$ − CH$_3$). Anal. Calcd. for $C_{26}H_{58}N_4O_4Al_2$: C, 57.33; H, 10.73; N, 10.29. Found: C, 57.25; H, 10.91; N, 10.48.

Single-Crystal X-ray Diffraction Studies for Complexes 1−4. The crystallographic measurements were performed at 296(2) K for all complexes **1**−**4** using a Bruker APEX II diffractometer with Mo Kα (λ = 0.71073 Å) radiation. Specimens of suitable quality and size were selected, mounted, and centered in the X-ray beam by using a video camera. The structures were solved by the direct method and refined by full-matrix least-squares methods using the SHELXTL[29] program package with anisotropic thermal parameters for all non-hydrogen atoms. Final refinement based on the reflections ($I > 2\sigma(I)$) converged at R_1 = 0.0486, wR_2 = 0.1168, and GOF = 1.014 for **1**; at R_1 = 0.0644, wR_2 = 0.2119, and GOF = 1.007 for **2**; at R_1 = 0.0522, wR_2 = 0.1170, and GOF = 1.009 for **3**; and at R_1 = 0.0603, wR_2 = 0.1676, and GOF = 1.068 for **4**.

Representative Procedure for Cycloaddition Reaction of CO$_2$ to Epoxide. The cycloaddition reaction of CO$_2$ to epoxide was carried out by charging a stirring bar, epoxide (10 mmol), aluminum compound (10 μmol), and cocatalyst (10 μmol) into a stainless steel autoclave. The autoclave was initial pressurized to 10 bar of CO$_2$ and was heated to the desired temperature. When the desired time was reached, the reactor was cooled and vented. A small sample of mixture was taken for ^{1}H NMR analysis.

RESULTS AND DISCUSION

The free ligands, $MeOCH_2CH_2NHCH_2CMe_2OH$ (**L1H**) and $Me_2NCH_2CH_2NHCH_2CMe_2OH$ (**L3H**), were synthesized by the reaction of isobutylene oxide with 2-methoxyethylamine and *N*,*N*-dimethylethylenediamine, respectively. Both ligands **L1H** and **L3H** are bidentate chelating ligands and contain a pendant $-CH_2CH_2OMe$ group and a pendant $-CH_2CH_2NMe_2$ attached to the nitrogen atom, respectively. Also, the ligands, **L2H$_2$** and **L4H$_2$**, were each produced by reacting of isobutylene oxide with **L1H** and **L3H** in a similar synthetic procedure for **L1H** and **L3H**. The obtained ligands **L2H$_2$** and **L4H$_2$** are tridentate ligands and have an extra pendant $-CH_2CH_2OMe$ group and a pendant $-CH_2CH_2NMe_2$ attached to the nitrogen atom, respectively.

A series of new dimeric Al complexes **1**−**4** were obtained with high yields (70−88%) in toluene, as illustrated in Scheme 1. In all cases, the synthesis of the aluminum complexes was achieved using inert atmosphere techniques. The new dimeric aluminum(III) complex **1** was prepared via simple reaction by adding a solution of 1 equiv of AlMe$_3$ dropwise to a solution of **L1H** in toluene at 0 °C, and the reaction mixture was stirred, at room temperature, for overnight, after which time the solvent and CH$_4$ were removed in vacuo. The other aluminum(III) complexes **2**−**4** were synthesized in a manner analogous to the procedure for **1**. Analytically pure samples were obtained as colorless crystals after the solvent remained at −15 °C in a refrigerator. Compounds **1**−**4** were not stable in air but thermally stable even at 130 °C. They are soluble in polar organic solvents and in toluene, but insoluble in hexanes. Compounds **1**−**4** were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{27}Al NMR spectroscopies and EI mass spectrometry, and also by elemental analysis and the single-crystal X-ray crystallographic method.

The molecular structures of **1**−**4** were determined by single-crystal X-ray diffraction analysis. Single crystals suitable for X-ray structural determination were obtained by cooling a solution of saturated toluene at −20 °C. The crystal structures for **1**−**4** are shown in Figure 1. In the solid state, the complexes have a dimeric Al$_2$O$_2$ four-membered ring with a center of symmetry. The two bridging O atoms link the two AlMe$_2$ for **1** and **3** and the two AlMe for **2** and **4**. Thus, the structures indicate that all four complexes are dinuclear with two five-coordinate aluminum centers via two-bridged oxygen. **1** and **3** have each of aluminum centers bonding to one N, two C atoms

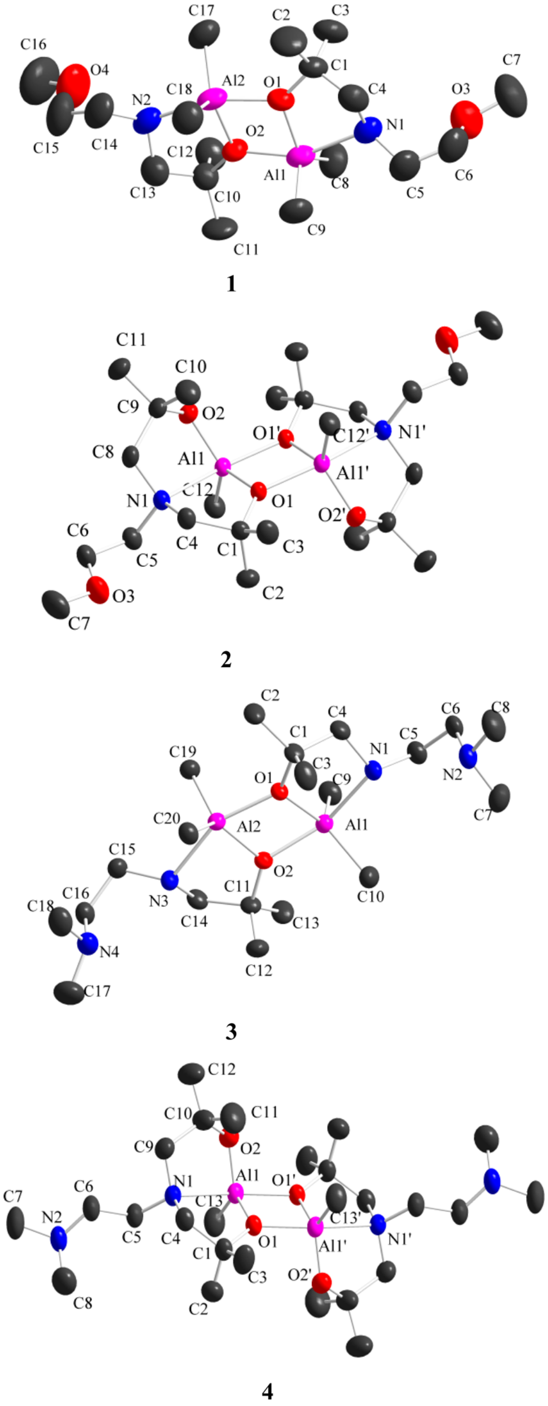


Figure 1. X-ray structures of **1**−**4** with thermal ellipsoids drawn at the 50% probability level. All H atoms are omitted for clarity.

of methyl groups, and two-bridged O atoms, whereas **2** and **4** possess aluminum centers bonding to one O, one N, one C of the methyl group, and two-bridged O atoms. The complexes have an inversion center (*i*) at the centroid of the Al_2O_2 ring plane; however, there is a slight asymmetry in the ring system. All complexes **1**−**4** have a noncoordinate pendant group such as $-CH_2CH_2OMe$ or $-CH_2CH_2NMe_2$ attached to the nitrogen atom. There are no direct Al1−Al2 interactions for **1**−**4**, and Al−O, Al−N, and Al−C bond distances are similar to those found in related pentacoordinate aluminum complexes.[30]

The distortion of the coordination around Al metal was determined by the trigonality parameter τ ($\tau = [\alpha - \beta]/60$, where α and β are the largest and next-largest interligand bond angles).[31] The trigonality parameter τ for the regular trigonal-bipyramidal (tbp) complexes is 1.0, and τ for square-pyramidal (sqp) complexes is 0. The τ values of **2** and **4** are 0.585 and 0.595, respectively, indicating the geometries around the Al center of both complexes, which are marginal tbp. There are two different τ values in each complex for **1** and **3**. The τ values with respect to **1** are 0.511 and 0.493, whereas the other τ values for **2** are 0.509 and 0.595 for each Al1 center and Al2 center. Therefore, the two aluminum complexes cannot be reasonably defined as having either geometry. They might be intermediate geometries between tbp and sqp.

The electron impact mass spectrum (70 eV) of **1**−**4** indicates dimeric behavior in the gas phase. The highest mass peaks, which are detected at $m/z = 406$ for **1**, $m/z = 518$ for **2**, $m/z = 430$ for **3**, and $m/z = 544$ for **4**, could be attributed to their dimeric structures. The absence of additional peaks in the EI-MS spectrum suggests that other species in toluene solution are absent or are present in undetectably low concentration. These results are well-matched with the dimeric solid-state structures shown in Figure 1.

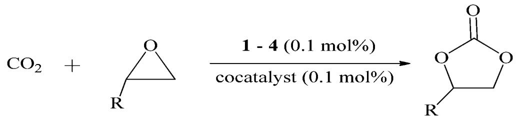
The ^1H and ^{13}C NMR spectra were in accord with the suggested structures, and all chemical shifts of the protons and carbon atoms were in the expected range. For all of the new dimeric aluminum compounds **1**−**4**, the ^1H NMR spectra showed characteristic shifts in contrast to each ligand. All complexes seem to have *pseudo*-C_2 symmetry because $-NCH_2$-CH_2OMe- and $-NCH_2CMe_2-$ methylene protons were split as two slightly broad peaks with couples of diastereotopic *AB* spin system for **1** and **2**. Also, broad peaks of $-NCH_2CH_2$-NMe_2- methylene protons and $-NCH_2CMe_2-$ methylene protons for **3** and **4** were observed. These features are very similar to those previously reported in our paper.[32] Since ^1H and ^{13}C NMR chemical shifts of pendant groups such as OMe and NMe_2 for **1**−**4** showed the similar shift with the corresponding ligands, pendant groups exist as noncoordinating and free mode.

To check whether compounds **1**−**4** indeed remain dinuclear in solution, ^{27}Al NMR experiments were carried out. In general, the ^{27}Al NMR chemical shift for organoaluminum compounds correlates with the coordination geometry and coordination number of the aluminum atom.[33] According to the reported literature,[32] the ^{27}Al NMR shifts of the tricoordinate, tetracoordinate, pentacoordinate, and hexacoordinate organoaluminum compounds could appear at 250−300 ppm, about 150 ppm, about 100 ppm, and 0 ppm, respectively. Two ^{27}Al NMR peaks in C_6D_6 for compounds **1**−**4**, a narrow peak at 93.3−98.6 ppm and a broad peak at about 62 ppm, were observed (aluminosilicate peak of NMR tube appeared at 62.5 ppm). The ^{27}Al NMR data between the four complexes change remarkably little. This is unsurprising between **1** and **3**, and between **2** and **4**; however, the unexpected small difference between **1**/**2** and **3**/**4** pairs was observed, though they have quite different chemical environments. Interestingly, the same dimeric characteristics for **1**−**4** were observed in the strongly coordinating solvent such as THF-d_8. The combined results for narrow peaks at 93.3−98.6 ppm and no large downfield shifts for O*Me* and N*Me*$_2$ peaks in ^1H and ^{13}C NMR affirm the dimeric behavior for compounds **1**−**4** in solution and a pentacoordinate tbp or sqp environment around the central Al atom.

To check whether the solution structures for complexes **1**−**4** were maintained during the cycloaddition reaction, we investigated ^{27}Al NMR experiments for **3**/propylene oxide, **3**/epichlorohydrin, **3**/tetrabutylammonium iodide (*n*-Bu_4NI), **3**/tetrabutylphosphonium bromide (TBPBr), **3**/PO/*n*-Bu_4NI, and **3**/PO/TBPBr systems. Three mixed components of **3**/PO/*n*-Bu_4NI and **3**/PO/TBPBr gave slightly downfield shifted signal, and others did not show any changes in ^{27}Al NMR chemical shift (see the Supporting Information). Thus, it seems that complexes **1**−**4** remain dinuclear in solution regardless of the presence of cocatalyst and/or epoxides.

The cycloaddition of CO_2 was performed without solvent using aluminum compounds **1**−**4** as catalysts in the presence of cocatalyst. The results are summarized in Table 1. We carried out the reaction at 70 °C under the condition of a fixed [Al]/[*n*-Bu_4NI] ratio of 1 and found that complex **3** had the highest TON value of 769 (Table 1, entries 1−4). Propylene oxide was easily converted into the cyclic carbonate with high selectivity

Table 1. Cycloaddition of CO_2 to Epoxides Using Complexes 1−4[j]



entry	cat.	cocat.[f]	R group[g]	T (°C)	TON[h]	selectivity (%)[i]
1	**1**[a]	*n*-Bu_4NI	Me	70	725	>99
2	**2**[a]	*n*-Bu_4NI	Me	70	598	>99
3	**3**[a]	*n*-Bu_4NI	Me	70	769	>99
4	**4**[a]	*n*-Bu_4NI	Me	70	659	>99
5	**3**[a]	DMAP	Me	70	79	>99
6	**3**[a]	PPNCl	Me	70	737	>99
7	**3**[a]	TBPBr	Me	70	843	>99
8	**3**[b]	TBPBr	Me	50	903	>99
9	**3**[c]	TBPBr	Me	100	833	>99
10	**3**[d]	TBPBr	Me	130	932	>99
11	**3**[a]	TBPBr	Ph	70	261	>99
12	**3**[a]	TBPBr	CH_2OPh	70	659	>99
13	**3**[e]	TBPBr	CH_2Cl	70	945	>99
14	[a]	*n*-Bu_4NI	Me	70	58	
15	[a]	TBPBr	Me	70	34	
16	[a]	PPNCl	Me	70	79	
17	[a]	DMAP	Me	70	0	

[j] Cycloaddition conditions: epoxide (10 mmol), CO_2 (10 bar), catalyst (10 μmol), cocatalyst (10 μmol). [a] Time = 24 h. [b] Time = 144 h. [c] Time = 13 h. [d] Time = 5 h. [e] Time = 15 h. [f] Tetrabutylammonium iodide (*n*-Bu_4NI), tetrabutylphosphonium bromide (TBPBr), bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), 4-dimethylaminopyridine (DMAP). [g] R = Me, propylene oxide; R = Ph, styrene oxide; R = CH_2OPh, 1,2-epoxy-3-phenoxypropane; R = CH_2Cl, epichlorohydrin. [h] Turnover number (TON) = (mol of PO consumed)/(mol of (co)catalyst). [i] Calculated by ^1H NMR spectral integration.

(>99%) without any polymerized products. To check the cocatalyst effect on the catalytic activity, four different kinds of cocatalysts, such n-Bu$_4$NI, TBPBr, bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), and 4-dimethylaminopyridine (DMAP), were used. As shown in Table 1, entries 3 and 5−7, TBPBr is superior compared with the three others. Moreover, catalyst **3** showed somewhat high activity in the presence of a salt-type cocatalyst, such as n-Bu$_4$NI, PPNCl, and TBPBr (entries 4, 6, and 7). However, catalyst **3** with the non-salt-type cocatalyst DMAP showed very low activity (entry 5).

Interestingly, cocatalyst n-Bu$_4$NI without **1**−**4** showed only a tenth of activity with a catalyst (entry 14). Other cocatalysts without catalysts showed the similar low activity (entries 15−17). In addition, the catalytic activity for **3** increases as the reaction temperature increases up to 130 °C (entries 7−10). Shorter reaction time is needed to reach the similar activity at elevated temperature. Interestingly, **3** did not give any poly(propylene)carbonate even at a low temperature of 50 °C. Complexes **1** and **3**, which have two Me groups per aluminum center, are better catalytic systems than the corresponding complexes **2** and **4** with a mono methyl group per aluminum. In addition, complexes **3** and **4** containing a pendant $-CH_2CH_2NMe_2$ group attached to nitrogen showed the higher activity than those **1** and **2** with a pendant $-CH_2CH_2OMe$ group did. Among four kinds of epoxides, such as propylene oxide, styrene oxide, 1,2-epoxy-3-phenoxypropane, and epichlorohydrin, the last one is the most active epoxide for the cycloaddition reaction (entries 7 and 11−13).

Oxo-bridged dimeric Al(III) complexes containing aromatic salen ligands as catalysts for the cycloaddition of CO_2 with epoxides were reported by North and co-workers.[23] Even though different conditions for the cycloaddition reaction were applied, their reported TON values are 47−820,[23] which are slightly lower than those for our systems. Compared with other metal catalysts, complexes **1**−**4** showed the moderate activities for the cycloaddition reaction. This result presumably comes from the fact that complexes **1**−**4** may have high activation energy to make a hexacoordinate intermediate with epoxides because the complexes remain dimeric in solution, as confirmed by ^{1}H and ^{27}Al NMR experiments.

■ CONCLUSION

Dimeric aluminum catalysts with multidentate aliphatic aminoethanol-based ligands were easily prepared, and their catalytic behaviors in the cycloaddition of CO_2 to epoxides were investigated. Complex **3** with NMe_2 pendant substituents showed the highest activity among the reported Al catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF file giving X-ray characterization of **1**−**4**, figures giving the ^{1}H, ^{13}C, and ^{27}Al NMR and EI-mass spectra for new compounds, and table of crystallographic data for complexes **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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