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New Highly Active Salen-based Aluminum Catalyst for the Coupling of Carbon Dioxide with Epoxides at Ambient Temperature

Won Hee Woo,^[a] Kyunglim Hyun,^[a] Yoseph Kim,^[a] Ji Yeon Ryu,^[b] Junseong Lee,^[b] Min Kim,^{*[a]} Myung

Hwan Park,*[c] and Youngjo Kim*[a]

Abstract: A novel aluminum complex, [(naph)salen]AIMe [(naph)salen N,N'-(2,3-naphthalene)bis(3,5dimethylsalicylideneiminato)], has been synthesized and fully characterized by NMR spectroscopy, high-resolution mass spectrometry, elemental analysis, and single-crystal X-ray diffraction. The complex exhibits square pyramidal geometry around the aluminum center in the solid-state structure, and it has a trigonality parameter (T) of 0.13. Comparison of the catalytic activity of [(naph)salen]AIMe with that of four related aluminum complexes containing tetradentate salen ligands with different bridging groups revealed that the naphthyl bridged salen-based aluminum complex, in conjunction with tetra(n-butyl)ammonium iodide as a cocatalyst, showed higher catalytic activity than the other complexes for the coupling of CO₂ with epoxides under the mild conditions of room temperature and 5 bar of CO₂ in 12 h. In addition, the new salen complex [(naph)salen]AIMe showed favorable features, such as requiring low catalyst loading (0.5 mol%) and broad epoxide substrate scope, including six terminal epoxides and three internal epoxides.

Introduction

Finding new catalytic systems for the coupling of CO₂ with epoxides to make cyclic carbonates, which have broad applications as aprotic solvents, electrolytes for lithium ion batteries, monomers for polymers, and pharmaceutical intermediates, is one of the most active research areas in CO2 conversion.^[1-5] A variety of catalytic systems have been reported for this transformation.^[1-5] Among these systems, non-toxic and earth-abundant aluminum-based catalysts for the conversion of CO₂ are one of the most significant systems.^[6-60] Bidentate phenoxides,^[6] bidentate benzotriazole pyrazole-based scorpionates,^[7-9] bidentate 8-hydroxyquinoline,^[10,11] tetradentate triphenolateamine,^[12-16] tetradentate porphyrin,^[17-21] tetradentate salen,^[22-55] salenac,^[56] salalen,^[57,58] tetradentate and

[a]	Department of Chemistry and BK21+ Program Research Team
	Chungbuk National University
	Cheongju, Chungbuk 28644, Republic of Korea
	E-mail: ykim@chungbuk.ac.kr
	http://omlab2005.chungbuk.ac.kr
[b]	Department of Chemistry
	Chonnam National University
	Gwangju 61186, Republic of Korea
[c]	Department of Chemistry Education, Chungbuk National University,
	Cheongju, Chungbuk 28644, Republic of Korea

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.xxxxx. bidentate/tridentate/tetradentate aliphatic aminoalcohols^[59,60] have all been used extensively as chelating ligands for aluminum-based catalysts. Among these ligands, tetradentate salen compounds are the most popular ligands for aluminum-based catalysts for the coupling of CO_2 with epoxides.^[22-55]



Figure 1. Structural representation of salen-based aluminum catalysts reported in the literature.

Figure 1 shows the simplified structure of the salen-based aluminum catalysts for the coupling of CO₂ with epoxides. Salen ligands are very versatile due to the many opportunities for facile modification at R¹, R², X, and Y. Theoretically, many substituents and groups could be introduced into salen ligands; however, most of these modifications in salen-based aluminum catalysts have been confined to the R¹, R², and X positions (Figure 1).^[22-55] In addition, the systematic tuning is limited only to -CH₂CH₂-, 1,2-C₆H₄, and (1*R*,2*R*)-cyclohexyl groups at bridging site Y.

Interestingly, salen-based aluminum complexes generally exist in either square pyramidal (sqp) or trigonal bipyramidal (tbp) geometries. The distortion of the coordination around the AI metal in pentacoordinated systems is given by the trigonality parameter τ (Tau). The τ value can be calculated by the equation $\tau = [\alpha - \beta]/60$, where α and β are the largest and next-largest interligand bond angles.^[61] The trigonality parameter τ for an ideal tbp complex is 1.0 and τ for an ideal sqp complex is zero.

 Table 1. T Values for some salen-based aluminum complexes.



Y	Х	тvalue	reference
4,5-dimethyl-1,2-phenylene	-CH ₂ CHMe ₂	0.14	62
4,5-dimethyl-1,2-phenylene	-OSiMe ₃	0.15	63
4,5-dimethyl-1,2-phenylene	-OSiPh₃	0.17	64
4,5-dimethyl-1,2-phenylene	-CI	0.18	63
-CH ₂ CH ₂ -	-OSiPh₃	0.40	62
-CH ₂ CH ₂ -	-OEt	0.45	64
-CH ₂ CH ₂ -	-OSiMe ₃	0.46	63
-CH ₂ CH ₂ -	-OPh	0.46	26
-CH ₂ CH ₂ -	-CH₃	0.47	62
(1 <i>R</i> ,2 <i>R</i>)-cyclohexyl	-N(SiMe ₃) ₂	0.55	61
(1 <i>R</i> ,2 <i>R</i>)-cyclohexyl	-OSiPh₃	0.74	62
-CH ₂ CH ₂ CH ₂ -	-Cl	0.77	63

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Table 1 clearly demonstrates how changing the salen ligand backbone changes the resulting coordination of the aluminum center.^[26,61-64] With fixed *tert*-butyl groups as substituents of the phenyl rings, the τ values strongly depend on the nature of the bridging backbones of the salen ligands but are independent of the type of the X substituents directly bound to the aluminum center. Rigid backbones such as phenylene prefer sqp geometries; however, flexible backbones such as -CH₂CH₂CH₂-favor tbp geometries. Thus, aluminum complexes with rigid backbones adopt sqp geometries in which tetradentate salen ligands occupy the base and the X group takes the apical position as shown in Figure 2.



Figure 2. Geometric dependence of Lewis acid catalysts.

Such complexes could act as good Lewis acid catalysts due to the existence of an apical vacant site opposite the X group. However, if the bridging group Y becomes flexible, aluminum complexes may have tbp geometries with no room for a substrate at the apical position, and then, they will be poor Lewis acid catalysts. Inspired by this situation, we hypothesized that a highly conjugated salen ligand might increase the rigidity of the bridging backbone brining the τ value close to zero, inducing sqp geometry around the aluminum center rather than a tbp environment.



Figure 3. Salen derivatives used in this study.

In this context, here, we report the synthesis and characterization of the aluminum complex **[(naph)salen]AIMe**, containing the naphthalene-bridged salen ligand **(naph)salen**, and its use as a catalyst for the coupling of CO_2 with epoxides under very mild conditions (room temperature, 5 bar of CO_2 , and 0.5 mol% catalyst loading). To the best of our knowledge, aluminum compound with naphthalene-bridged salen derivatives in the Y position have never been reported. As shown in

Figure 3, we also investigated the effect of **(naph)salen** ligand coordinated to the aluminum center on the coupling reaction. To gain insight into the degree of influence of the rigid backbone, we systematically synthesized aluminum compounds containing four different kinds of salen derivatives, namely, **(Me₂Ph)salen**, **(Ph)salen**, **(Cl₂Ph)salen**, and **salen**. Their catalytic activities were compared with that of **[(naph)salen]AIMe**.

Results and Discussion



Scheme 1. Synthetic route to [(naph)salen]AIMe.

As shown in Scheme 1, the **(naph)salenH**² ligand is synthesized *via* the simple dehydration reaction of 2,3diaminonaphthalene with two equivalents of 2-hydroxy-3,5dimethylbenzaldehyde in ethanol. In a manner analogous to what was used in the synthesis of **(naph)salenH**₂, four other salen derivatives, namely, **salenH**₂,^[65] **(phen)salenH**₂, **(Me2phen)salenH**₂, and **(Cl2phen)salenH**₂, were prepared from 2-hydroxy-3,5-dimethylbenzaldehyde and the corresponding diamines (ethylenediamine, 1,2-phenylenediamine, 4,5dimethylphenylene-1,2-diamine, and 4,5-dichlorophenylene-1,2diamine, respectively).

The direct reaction of (naph)salenH₂ with AIMe₃ proceeds rapidly with evolution of 2 equiv. of methane to give the target compound [(naph)salen]AIMe in good yield (86%) as illustrated in Scheme 1. Although the reaction is exothermic and fast, reaction time of approximately 12 h was required to reach the maximum yield. The other aluminum complexes, (salen)AIMe, [(phen)salen]AIMe, [(Me₂phen)salen]AIMe, and [(Cl₂phen)salen]AIMe, were synthesized in a manner analogous to the synthesis of [(naph)salen]AIMe. In all cases, the synthesis of the aluminum complexes was achieved using inert atmosphere techniques. The complexes were obtained in excellent yields ranging from 82 to 97%, and although they are not stable in air, they are thermally stable even at 130°C. Generally, salen-based aluminum complexes are known to have poor solubility in common organic solvents.^[26,61-64] Thus, many salen-based aluminum catalysts for the coupling of CO2 and epoxides possess a tert-butyl group at the 3-position of the phenolate ring to improve their solubility in epoxides, which is a common solvent for this transformation.[22-55] Until now, aluminum complexes containing a methyl group at the 3-position of the phenolate ring of the salen ligands have never been reported as catalysts for the cycloaddition of CO₂ to epoxides. Interestingly, all aluminum complexes synthesized in this study are freely soluble in polar organic solvents and in toluene, but they are insoluble in hexanes.

All aluminum complexes were characterized by ¹H and ¹³C NMR spectroscopies, HRMS spectrometry, elemental analysis

and by single-crystal X-ray crystallography using the same method as was described for **[(naph)salen]AIMe**. The spectroscopic data for the five aluminum complexes are consistent with monomeric species. The ¹H and ¹³C NMR spectra were in good agreement with the expected structures, and all chemical shifts of the protons and carbons were in the expected ranges. ¹H NMR spectra of aluminum complexes show the absence of signals at approximately 13 ppm for -OH, confirming the successful formation of AI complexes coordinated to salen–based ligand. In addition, a strongly shielded aluminum–bound methyl resonance at about -0.4 ppm in the ¹H NMR spectrum further confirms the successful complexation.

The molecular structure of [(naph)salen]AIMe was determined by single-crystal X-ray diffraction analysis. X-ray quality crystals were obtained from an NMR tube containing [(naph)salen]AIMe in C₆D₆ at room temperature. The solid-state structure for [(naph)salen]AIMe shows that the central aluminum atom is in a geometry that is best described as slightly distorted sop with trans basal O-Al-N angles of 142.50(10)° and 150.30(11)° as shown in Figure 4. The basal nitrogen and oxygen atoms are coplanar within 0.06 Å, and the aluminum atom is located 0.54 Å above this base plane, which is very similar what has been observed in the related salen-based aluminum complexes.^[26,61-64,66,67] The short AI-O bond distances of 1.794(2) and 1.7972(19) Å and the long AI-N bond lengths of 2.026(2) and 2.049(2) Å suggest a strong bond between the O atoms and the AI atom and a weak interaction between the N atoms and the AI atom upon complexation. The AI-C bond distance of 1.954(3) Å is within the range found in previously reported methylaluminum complexes.[58,59,62,66,67] The apical site is occupied by the methyl substituent. The T value of [(naph)salen]AIMe is 0.13, indicating a geometry around the AI center that is close to sqp. Furthermore, [(naph)salen]AIMe has one of the smallest T value among all structurally characterized salen-aluminum complexes.[26,58,61-64,66,67]



Figure 4. X-ray crystal structure of [(naph)salen]AIMe (50% thermal ellipsoids). For clarity, all H atoms are omitted.

The influence of cocatalysts on the coupling of CO_2 with propylene oxide was investigated using **[(naph)salen]AIMe** as the catalyst in conjunction with six different cocatalysts, and the results are shown in Table 2. We carried out the reaction at ambient temperature (25°C) with a fixed [propylene oxide]/[AI] ratio of 200, CO_2 pressure of 5 bar, and reaction time of 12 h. Propylene oxide was easily converted into the cyclic carbonate with high selectivity (>99%) and without any polymerized products. As shown in entry 4 of Table 3, cocatalyst *n*-Bu₄NI gave better conversion and turnover number than the other five cocatalysts. The catalyst **[(naph)salen]AIMe** showed somewhat higher activity in the presence of salt cocatalysts (entries 1-5); however, the non-salt-type cocatalyst DMAP showed very low activity (entry 6). As expected, tetrabutylammonium salts showed that the activity increased as the nucleophilicity of the halide increased (Cl⁻ < Br⁻ < l⁻) (entries 3-5).

Table 2. Influence of cocatalysts on the catalytic activity of [(naph)salen]AlMe at room temperature.^a

بر	+ 00 -	0.5 mol% [(naph)salen]AlMe 0.5 mol% cocatalyst	-	
\square	. 002	25ºC, 5 bar CO ₂ , 12 h	Ĭ-Ţ	
Entry	Cocatalyst	Yield [%] ^b	TON°	
1	PPNCI	72	144	
2	(n-Bu)4NCI	46	92	
3	(n-Bu) ₄ NBr	83	166	
4	(<i>n</i> -Bu)₄NI	87	174	
5	(<i>n</i> -Bu)₄PBr	81	162	
6	DMAP	17	33	

^a [(naph)salen]AIMe 0.5 mol%, cocatalyst 0.5 mol%, propylene oxide 10 mmol, CO₂ pressure 5 bar, room temperature (25°C), time = 12 h; ^b obtained yield; ^c turnover number.

With the optimized catalytic system [(naph)salen]AIMe/(n-Bu)₄NI in hand, we next moved to investigate the optimum concentration of catalyst and cocatalyst at a fixed temperature (25°C), CO₂ pressure (5 bar), and time (12 h), as shown in Table 3. At a catalyst and cocatalyst loading of 0.5 mol%, 87% yield of the cyclic propylene carbonate was achieved after 12 h (entry 1). experiments involving Control the use of either [(naph)salen]AIMe or (n-Bu)₄NI alone gave only 7% or 5% yield, respectively (entries 2 and 3), further demonstrating the synergistic effect of using [(naph)salen]AIMe and (n-Bu)₄NI together. In addition, if the catalyst and cocatalyst loading is reduced by half, but the ratio of catalyst to cocatalyst remains 1:1, the yield of cyclic propylene carbonate decreased from 87% to 58% (entry 4). Therefore, we decided that the optimal loading for catalyst and cocatalyst was 0.5 mol% since it afforded the cyclic propylene carbonate in a yield of 87% after 12 h.

Table 3. Optimization of the synthesis of cyclic propylene carbonate using [(naph)salen]AlMe and $(n-Bu)_4NI.^a$

8	[(naph)salen]AlMe (n-Bu) ₄ Nl	
	25ºC, 5 bar CO ₂ , 12 h	<mark>کـر</mark>

Entry	[(naph)salen]AIMe [mol%]	(<i>n</i> -Bu) ₄ NI [mol%]	Yield [%] ^b
1	0.5	0.5	87
2	0.5	0	7
3	0	0.5	5
4	0.25	0.25	58

 a propylene oxide 10 mmol, CO_2 pressure 5 bar, room temperature (25°C), time = 12 h; b obtained yield.

Having determined that the optimal coupling conditions are 0.5 mol% of **[(naph)salen]AlMe** and (*n*-Bu)₄NI at 25°C and 5 bar CO₂ pressure for 12 h, a series of salen-based aluminum catalysts, **(salen)AlMe**, **[(phen)salen]AlMe**, **[(Me2phen)salen]AlMe**, and **[(Cl2phen)salen]AlMe**, were explored as catalysts and their activities were compared with that of **[(naph)salen]AlMe**. The results are listed in Table 4. Among the five catalysts, **[(naph)salen]AlMe** showed the

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highest turnover number of 174, which was 2.5 times the turnover number obtained using (salen)AIMe. As expected, [(naph)salen]AIMe and (salen)AIMe have the most rigid and the most flexible bridging backbones, respectively (entries 1 and 5). Interestingly, the activity of [(phen)salen]AIMe, which has a more rigid backbone than (salen)AIMe, is almost twice that of (salen)AIMe (entry 2). Electron-donating and -withdrawing substituents introduced into the bridging backbone have a negative effect on activity, reducing TON to 98 and 120, respectively (entries 3 and 4). As expected, the more Lewis acid catalyst [(Cl₂phen)salen]AIMe showed higher catalytic activity than [(Me₂phen)salen]AIMe, which is a weaker Lewis acid.

Table 4. Comparison of catalytic activities using aluminum complexes in conjunction with (n-Bu)₄NI at room temperature.^a

	⁰ + CO₂ −	0.5 mol 0.5 mol	% Al catalyst % (<i>n</i> -Bu) ₄ NI	→ ⁰
	Λ	25 0, 5	$Dar CO_2, 12 II$	\backslash
Entry	Catalyst		Yield [%] ^b	TON℃
1	[(naph)salen]A	IMe	87	174
2	[(phen)salen]A	IMe	78	157
3	[(Me2phen)sale	n]AlMe	49	98
4	[(Cl₂phen)saler	n]AIMe	60	120
5	(salen)AIMe		36	72

 a Catalyst 0.5 mol%, (*n*-Bu)_4NI 0.5 mol%, propylene oxide 10 mmol, CO₂ pressure 5 bar, room temperature (25°C), time = 12 h; b obtained yield; c turnover number.

We next moved to investigate the substrate scope using 0.5 mol% [(naph)salen]AIMe in conjunction with an equal amount of (*n*-Bu)₄NI (Table 5). Substrates include six terminal epoxides, namely, propylene oxide (entry 1), 1,2-epoxyhexane (entry 2), styrene oxide (entry 3), methyl glycidyl ether (entry 4), tert-butyl glycidyl ether (entry 5), and 1,2-epoxy-3-phenoxypropane (entry 6) and three internal epoxides, namely, 1,2-epoxy-2methylpropane (entry 7), 2,3-epoxybutane (entry 8), and cyclohexene oxide (entry 9). The coupling reactions were carried out at room temperature (25°C) for terminal epoxides and 120°C for internal epoxides. In the case of epoxides with alkyl and phenyl substituents, the simplest epoxide showed the highest conversion (entries 1-3). This finding means the activity is greatly impacted by chain length and steric hindrance. When a heteroatom was introduced at the 3-position, the high reactivity of the catalyst system was maintained (entries 1 and 4). Like the trend for epoxides with no heteroatom (entries 1-3), a quick loss of reactivity for epoxides with -CH2O^tBu and -CH2OPh substituents was observed (entries 5 and 6). Not surprisingly, internal epoxides such as 1,2-epoxy-2-methylpropane (entry 7), 2,3-epoxybutane (entry 8), and cyclohexene oxide (entry 9) exhibited low activities. Among internal epoxides, cyclohexene oxide showed the highest 60% isolated yield within 12 h at 120°C. For the 1,2-disubstituted epoxides, we used a mixture of trans- and cis-2,3-epoxybutane (entry 8) and cis-cyclohexene oxide (entry 9) for the coupling reaction. Generally, cyclic carbonates obtained from 1,2-disubstituted epoxides have the retention of configuration via the combination of two S_N2 reaction taking place at the ring-opening and ring-closure stage of the coupling reaction.^[12,68-70] As shown in Figures S44-S47 of the Supporting Information, an 83:17 miture of trans/cis isomers of 4,5-dimethyl-1,3-dioxolan-2-one (entry 8) and >99% pure *cis*-hexahydrobenzo[d][1,3]dioxol-2-one with the retained original configuration of epoxide (entry 9) was obtained.

	0 -1	0.5 mol%	len]AlMe) ₄ Nl)	
Ŕ	R^3 R^1 R^2	5	bar CO ₂		R^1	–R ³ R ²
Entry	R ¹	R ²	R ³	Temp (°C)	Time (h)	Yield [%] ^ь
1	Н	–CH₃	н	25	12	87
2	Н	-CH ₂ CH ₂ CH ₂ CH ₃	н	25	24	86
3	н	–Ph	н	25	36	91
4	н	-CH ₂ OMe	н	25	12	80
5	н	-CH ₂ O ^t Bu	н	25	24	95
6	н	-CH ₂ OPh	н	25	48	51
7	Н	–CH₃	–CH₃	120	24	39
8	-CH ₃	–CH₃	н	120	24	47
9	-CH	H ₂ CH ₂ CH ₂ CH ₂ -	н	120	24	60

^a [(naph)salen]AIMe 0.5 mol%, (n-Bu)₄NI 0.5 mol%, epoxide 10 mmol, CO₂ pressure 5 bar; ^b obtained yield.

Up to now, many aluminum complexes containing salenbased ligands used as catalysts for the coupling of CO₂ with epoxides have been reported in the literature.^[22-55] However, compared to the conditions developed in this study, previously reported reaction conditions for this transformation are much harsher. Compared with other metal catalysts, the new salen-based aluminum compound **[(naph)salen]AIMe** showed moderate activities for this cycloaddition reaction. This result presumably comes from the fact that **[(naph)salen]AIMe** with a rigid backbone may have sqp geometry around the aluminum center, which can easily form hexa-coordinate intermediate with epoxides.

Conclusions

We prepared the novel aluminum compound [(naph)salen]AlMe, which has a naphthalene-bridged backbone between modified salicyliminato groups, and it has a trigonality parameter (T) of 0.13. This naphthalenebridged aluminum catalyst showed good catalytic activity in the coupling of CO₂ with propylene oxides at ambient temperature (25°C) under the mild condition of a fixed [propylene oxide]/[Al] ratio of 200, CO₂ pressure of 5 bar, and reaction time of 12 h. [(Naph)salen]AlMe demonstrated much higher catalytic activities than well-known ethylenebridged (salen)AIMe under the same reaction conditions. Using the [(naph)salen]AIMe/(n-Bu)₄NI catalytic system, a broad scope of terminal and internal epoxides were transformed to cyclic carbonates under mild conditions.

Experimental Section

General Considerations. All reactions of air- and moisture-sensitive materials were carried out under a nitrogen atmosphere using standard

Schlenk-type glassware on a dual manifold Schlenk line in a glove box.^[71,72] Nitrogen was deoxygenated using an activated Cu catalyst and dried with Drierite.^[73] All chemicals were purchased from commercial sources (purity > 99%) and used as received unless otherwise indicated. All solvents such as toluene and *n*-hexane, were dried by distillation from sodium/benzophenone ketyl or CaH₂ under a nitrogen atmosphere and stored over activated molecular sieves (4 Å). Carbon dioxide (99.999%) was used as received without further purification. CDCl₃ and C₆D₆ were 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 ¹³C NMR spectra were recorded at ambient temperature on a Bruker DPX-500 MHz NMR spectrometer using standard parameters. All chemical shifts are reported in δ and referenced to the residual CDCl₃ (δ 7.24 for ¹H NMR; δ 77.00 for ¹³C NMR) and C₆D₆ (δ 7.16 for ¹H NMR; δ 128.06 for ¹³C NMR). Elemental analyses were performed with EA 1110-FISONS analyzer. High-resolution mass spectra (HRMS) were acquired on a high resolution Q-TOF mass spectrometer (ionization mode: ESI).

Synthesis. N,N'-ethylenebis(3,5-dimethylsalicylideneimine) (salenH₂) was prepared according to the literature procedures.^[65]

General Synthesis of Salen Compounds. The appropriate corresponding diamine (5.0 mmol) was added to a stirred solution of 2–hydroxy-3,5-dimethylbenzaldehyde (1.50 g, 10.0 mmol) in 20 mL of ethanol at room temperature. The reaction mixture was allowed to reflux overnight, cooled, and filtered. The resulting residue was washed with cold ethanol (3 × 10 mL), and then dried in vacuo to afforded the desired products.

Data for **salenH**₂.^[65] yellow solid (1.35 g, 83%). ¹H NMR (CDCl₃): δ 13.2 (br, 2H, -OH), 8.27 (s, 2H, ArC*H*=N–), 6.97 (s, 2H, Ar–*H*), 6.84 (s, 2H, Ar–*H*), 3.90 (s, 4H, =NC*H*₂–), 2.22 (s, 6H, Ar–*M*e),2.21 (s, 6H, Ar– *M*e). ¹³C NMR (CDCl₃): δ 166.7 (ArCH=N–), 157.1, 134.5, 129.2, 127.2, 125.7 117.7 (*Ar*), 60.00 (=NCH₂–), 20.42 (Ar–*M*e), 15.55 (Ar–*M*e).

Datafor*N,N*'-phenylenebis(3,5-dimethylsalicylideneimine)[(phen)salenH₂]: yellow solid (1.58 g, 85%). ¹H NMR (CDCl₃): δ 12.9 (br,2H, -OH), 8.54 (s, 2H, ArCH=N–), 7.31 (m, 2H, Ar–H), 7.18 (m, 2H, Ar–H),7.05 (s, 2H, Ar–H), 7.00 (s, 2H, Ar–H), 2.26 (s, 6H, Ar–Me), 2.24 (s,6H, Ar–Me). ¹³C NMR (CDCl₃): δ 163.48 (ArCH=N–), 157.6, 140.2, 136.0,135.2, 129.9, 127.4, 126.1, 121.4, 118.4 (Ar), 20.45 (Ar–Me), 19.62 (Ar–Me),15.65 (Ar–Me). HRMS *m*/z calcd for [C₂₄H₂₄N₂O₂ + H] 373.1916.Found: 373.1911.

Data for *N*,*N*^L(4,5-dimethylphenylene)bis(3,5-dimethylsalicylideneimine) **[(Me₂phen)salenH₂**]: yellow solid (1.66 g, 83%). ¹H NMR (CDCl₃): δ 13.1 (br, 2H, –OH), 8.54 (s, 2H, ArCH=N–), 7.03 (s, 2H, Ar–H), 6.99 (s, 2H, Ar–H), 6.97 (s, 2H, Ar–H), 2.30 (s, 6H, Ar–Me), 2.26 (s, 6H, Ar–Me), 2.24 (s, 6H, Ar–Me). ¹³C NMR (CDCl₃): δ 163.5 (ArCH=N–), 157.6, 140.2, 136.0, 135.2, 129.9, 127.4, 126.1, 121.4, 118.4 (*Ar*), 20.45 (Ar–*Me*), 19.62 (Ar–*Me*), 15.65 (Ar–*Me*). HRMS *m*/*z* calcd for [C₂₆H₂₈N₂O₂ + H] 401.2229. Found: 401.2224.

Data for *N,N*-(4,5-dichlorophenylene)bis(3,5-dimethylsalicylideneimine) [(Cl₂phen)salenH₂]: orange solid (1.72 g, 78%). ¹H NMR (CDCl₃): δ 12.5 (br, 2H, –O*H*), 8.51 (s, 2H, ArC*H*=N–), 7.27 (s, 2H, Ar–*H*), 7.07 (s, 2H, Ar–*H*), 7.00 (s, 2H, Ar–*H*), 2.26 (s, 6H, Ar–*Me*), 2.23 (s, 6H, Ar–*Me*). ¹³C NMR (CDCl₃, 125.03 MHz): δ 165.2 (ArCH=N–), 157.7, 142.3, 136.3, 130.6, 130.3, 127.8, 126.5, 121.7, 118.0 (*Ar*), 20.44 (Ar–*Me*), 15.62 (Ar– Me). HRMS m/z calcd for $[C_{24}H_{24}Cl_2N_2O_2 + H]$ 441.1136. Found: 441.1131.

Data for N,N'-(2,3-naphthalene)bis(3,5-dimethylsalicylideneimine)[(naph)salenH₂]: orange solid (1.52 g, 72%). ¹H NMR (CDCl₃): δ 12.9 (br, 2H, -O*H*), 8.65 (s, 2H, ArC*H*=N-), 7.84 (m, 2H, Ar-*H*), 7.52 (s, 2H, Ar-*H*), 7.47 (m, 2H, Ar-*H*), 7.07 (s,2H, Ar-*H*), 7.05 (s,2H, Ar-*H*), 2.28 (s, 6H, Ar-*Me*), 2.26 (s, 6H, Ar-*Me*). ¹³C NMR (CDCl₃): δ 164.4 (ArCH=N-), 157.8, 143.2, 135.7, 132.8, 130.1, 127.8, 126.3, 118.4, 117.1 (*A*r), 20.48 (Ar-*Me*), 15.70 (Ar-*Me*). HRMS *m*/*z* calcd for [C₂₆H₂₆N₂O₂ + H] 423.2072. Found: 423.2067.

General Synthesis of (salen)AlMe Compounds. AlMe₃ (0.33 mL of 0.5 M toluene solution, 0.65 mmol) was added to a stirred solution of the corresponding salen ligand (0.5 mmol) in toluene at 0°C. The mixture was allowed to warm to room temperature and was left to stir overnight. The volatiles were removed under vacuum, and the residue was recrystallized from toluene at -15° C to give the desired products.

Datafor[ethylenebis(3,5-dimethylsalicylideneiminato)-
κ*N*,*N'*,O,O]methylaluminum (III) ((salen)AIMe): ivory solid (0.15 g, 82%).¹H NMR (C₆D₆): δ 7.34 (s, 2H, ArC*H*=N-), 7.05 (s,2H, Ar-*H*), 6.58 (s, 2H,
Ar-*H*), 3.06 (m, 2H, =NC*H*₂-), 2.58 (s, 6H, Ar-*Me*), δ 2.49 (m, 2H,
=NC*H*₂-), 2.20 (s, 6H, Ar-Me), -0.44 (s, 3H, Al-*Me*). ¹³C NMR (CDCl₃): δ
168.3 (ArCH=N-), 163.0, 137.5, 130.8, 129.8, 124.5, 117.6 (*Ar*), 54.86
(=NCH₂-), 20.41, 16.14 (Ar-*Me*). HRMS *m/z* calcd for [C₂₁H₂₅AIN₂O₂ +
Na] 387.1629. Found: 387.1624. Anal. Calcd for C₂₁H₂₅AIN₂O₂: C, 69.21;
H, 6.92; N, 7.69. Found: C, 69.16; H, 6.94; N, 7.72.

Datafor[phenylenebis(3,5-dimethylsalicylideneiminato)-
κ*N,N'*,O,O']methylaluminum (III) (**[[phen)salen]AIMe**): yellow solid (0.20
g, 97%). ¹H NMR (C₆D₆): δ 8.00 (s, 2H, ArC*H*=N–), 7.09 (s,2H, Ar–*H*),
6.90 (m, 2H, Ar–*H*), 6.82 (m, 2H, Ar–*H*), 6.95 (s, 2H, Ar–*H*), 2.61 (s, 6H,
Ar–Me), 2.19 (s, 6H, Ar–*Me*), -0.40 (s, 3H, Al–*Me*). ¹³C NMR (CDCl₃): δ
164.1 (ArCH=N–), 161.3, 139.1, 138.8, 131.1, 130.6, 128.3, 125.3, 117.7,
116.1 (*Ar*), 20.46, 16.16 (Ar–*Me*). HRMS *m*/*z* calcd for [C₂₅H₂₅AIN₂O₂ +
Na] 435.1629. Found: 435.1624. Anal. Calcd for C₂₅H₂₅AIN₂O₂: C, 72.80;
H, 6.11; N, 6.79. Found: C, 72.76; H, 6.05; N, 6.88.

Data for [(4,5-dimethylphenylene)bis(3,5-dimethylsalicylideneiminato)κ*N*,*N'*,O,O]methylaluminum (III) (**[(Me₂phen)salen]AIMe**): yellow solid (0.20 g, 91%). ¹H NMR (C₆D₆): δ 8.05 (s, 2H, ArC*H*=N–), 7.10 (s, 2H, Ar– *H*), 6.73 (s, 2H, Ar–*H*), 6.67 (s, 2H, Ar–*H*), 2.64 (s, 6H, Ar–*Me*), 2.21 (s, 6H, Ar–Me), 1.98 (s, 6H, Ar–*Me*), -0.35 (s, 3H, Al–*Me*). ¹³C NMR (C₆D₆): δ 164.6 (Ar*C*H=N–), 160.4, 138.6, 137.1, 136.8, 131.3, 130.8, 124.6, 118.0, 117.0 (*Ar*), 20.50, 19.88, 16.59 (Ar–*Me*). HRMS *m/z* calcd for [C₂₇H₂₉AIN₂O₂ + Na] 463.1942. Found: 463.1937. Anal. Calcd for C₂₇H₂₉AIN₂O₂: C, 73.62; H, 6.64; N, 6.36. Found: C, 73.67; H, 6.70; N, 6.42.

Data for [(4,5-dichlorophenylene)bis(3,5-dimethylsalicylideneiminato)- κ *N*,*N'*,O,O]methylaluminum (III) (**[(Cl₂phen)salen]AIMe**): orange solid (0.21 g, 87%). ¹H NMR (C₆D₆): δ 7.58 (s, 2H, ArC*H*=N–), 7.07 (s, 2H, Ar– *H*), 6.84 (s, 2H, Ar–*H*), 6.56(s, 2H, Ar–*H*), 2.57 (s, 6H, Ar–*Me*), 2.18 (s, 6H, Ar–Me), –0.45 (s, 3H, Al–*Me*). ¹³C NMR (C₆D₆): δ 164.7 (ArCH=N–), 161.8, 139.7, 138.4, 132.0, 131.3, 130.7, 125.8, 118.0, 117.5 (*A*r), 20.48, 16.11 (Ar–*Me*). HRMS *m*/*z* calcd for [C₂₅H₂₃AlCl₂N₂O₂ + Na] 503.0850. Found: 503.0844. Anal. Calcd for C₂₅H₂₃AlCl₂N₂O₂: C, 62.38; H, 4.82; N, 5.82. Found: C, 62.44; H, 4.86; N, 5.79.

Data for [(2,3-naphthalene)bis(3,5-dimethylsalicylideneiminato)κ*N*,*N*,*O*,*O*]methylaluminum (III) (**[(naph)salen]AlMe**): orange solid (0.20

g, 86%). ¹H NMR (C₆D₆): δ 8.08 (s, 2H, ArC*H*=N–), 7.61 (m, 2H, Ar–*H*), 7.32 (m, 2H, Ar–*H*), 7.19 (s, 2H, Ar–*H*), 7.10 (s, 2H, Ar–*H*), 6.70 (s, 2H, Ar–*H*), 2.62 (s, 6H, Ar–Me), 2.21 (s, 6H, Ar–*Me*), -0.31 (s, 3H, Al–*Me*). ¹³C NMR (C₆D₆): δ 165.3 (ArCH=N–), 162.6, 139.2, 138.8, 133.1, 131.4, 131.0, 126.7, 124.8, 118.1, 114.2 (*A*r), 20.48, 16.60 (Ar–*Me*). HRMS *m*/*z* calcd for [C₂₉H₂₇AlN₂O₂ + Na] 485.1786. Found: 485.1780. Anal. Calcd for C₂₉H₂₇AlN₂O₂: C, 75.31; H, 5.88; N, 6.06. Found: C, 75.38; H, 5.84; N, 6.13.

X-ray Crystallography. Single crystals suitable for X-ray diffraction analysis were obtained from NMR tubes containing **[(naph)salen]AlMe** dissolved in C₆D₆. The obtained crystal was coated with Paratone oil to maintain the crystallinity of the complex and mounted on the end of a glass capillary. A Bruker D8QUEST CCD area detector diffractometer with Mo-K α (λ = 0.71073 Å) radiation was used for the crystallographic measurements. The structures were solved by the direct method and all non-hydrogen atoms were subjected to anisotropic refinement by a full-matrix least–squares method *F*² using the SHELXTL/PC program package.^[74] Hydrogen atoms were geometrically calculated by the refinement of corresponding C atoms with isotropic thermal parameters. Final refinement based on the reflections ($l > 2\sigma(l)$) converged at $R_1 = 0.0560$, $wR_2 = 0.1217$, and GOF = 1.044 for **[(naph)salen]AlMe** (See Table 6).

Representative procedure for the coupling of CO₂ to epoxide. The coupling reaction of CO₂ to an epoxides was carried out by charging a stainless steel autoclave with a stirring bar, epoxide (10 mmol), and the aluminum catalyst (10 µmol). The autoclave was initially pressurized to 10 bar of CO₂ 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 ¹H NMR analysis.

Table 6. Crystallographic data for [(naph)salen]AIMe.

, , , ,	
CCDC #	1564307
Chemical formula	C ₂₉ H ₂₇ AIN ₂ O ₂
Formula weight	462.50
Crystal system	Monoclinic
Space group	P21/c
a (Å)	9.6244(9)
b (Å)	22.3211(19)
<i>c</i> (Å)	11.3645(10)
lpha (deg)	90.00
eta (deg)	101.390(6)
γ(deg)	90.00
V (Å ³)	2393.3(4)
Z	4
d _{calcd} (g/cm ³)	1.284
<i>F</i> (000)	976
Reflections collected	27192
# of independent reflections	4208 [R(int) = 0.1043]
# of parameters	312
$R_1(I > 2\sigma(I))^a$	0.0560
$wR_2(l > 2\sigma(l))^b$	0.1217
$GOF(I > 2\sigma(I))$	1.044
^a $R_1 = \Sigma F_0 - F_c / \Sigma F_0 $, ^b $wR_2 = \{\Sigma F_0 = \Sigma F_0 \}$	$w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

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Keywords: CO₂ fixation • Cyclic carbonate • Aluminum catalyst • Salen • Mild condition

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Novel naphthyl bridged salen-based aluminum complex in conjunction with tetra(*n*-butyl)ammonium iodide as a cocatalyst can effectively couple of carbon dioxide and epoxide under the condition of room temperature and low catalyst loading of 0.5 mol% within 12 h.



Won Hee Woo, Kyunglim Hyun, Yoseph Kim, Ji Yeon Ryu, Junseong Lee, Min Kim,* Myung Hwan Park,* and Youngjo Kim*

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New Highly Active Salen-based Aluminum Catalyst for the Coupling of Carbon Dioxide with Epoxides at Ambient Temperature