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Chiral Amido-Oxazolinate Zinc Complexes for Asymmetric Alternating Copolymerization of CO_2 and Cyclohexene Oxide

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Supporting Information

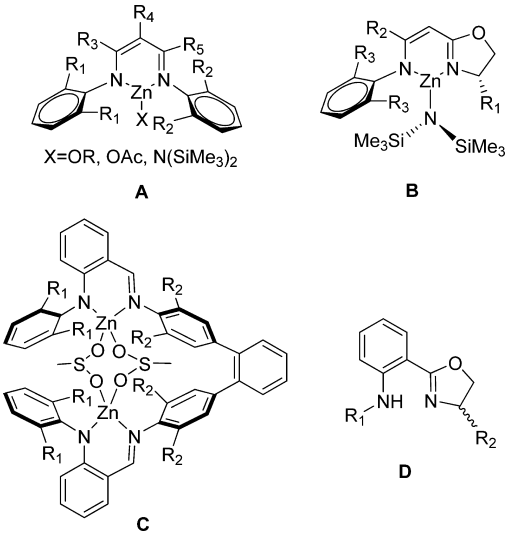
ABSTRACT: The synthesis and characterization of a series of chiral zinc complexes (L^{1a-m})ZnN($SiMe_3$)$_2$ (**2a−m**) with C_1-symmetric amido-oxazolinate ligands (HL^{1a-m} = 2-(2′-R_1NH)phenyl-4-R_2-oxazoline) have been described. Single-crystal X-ray crystallographic studies confirm that **2a** (R_1 = 2,6-dimethylphenyl, R_2 = (*S*)-^{i}Pr) and **2d** (R_1 = 2,6-dimethylphenyl, R_2 = (*R*)-^{i}Bu) are three-coordinate, mononuclear complexes, and **2k** (R_1 = PhCO, R_2 = (*S*)-^{i}Pr) exists as an amide oxygen-bridged dimer in the solid state with zinc in a distorted tetrahedral geometry. These complexes are viable initiators for alternating copolymerization of carbon dioxide (CO_2) and cyclohexene oxide (CHO), yielding poly(cyclohexene carbonate) (PCHC) with good to high carbonate linkage and moderate molecular weights and PDI values, depending on the substituents. The PCHCs produced are typically isotactic, containing up to 72% *m*-centered tetrads by **2h** (R_1 = 2,6-diisopropylphenyl, R_2 = (*R*)-^{i}Bu), and a rare case of syndiotactic PCHC (57% *r*-centered tetrads) is obtained with **2j** (R_1 = (*R*)-1-(1-naphthyl)ethyl), R_2 = (*R*)-^{i}Bu). The asymmetric induction is generally low, with up to 71% *SS* unit in the main chain of the produced PCHCs.

INTRODUCTION

Utilization of carbon dioxide (CO_2) as a renewable C_1 feedstock has attracted increased interest due to its low cost, nontoxicity, and availability in nature and from many industrial processes.[1] Given its thermodynamic and kinetic stability, one approach is to couple CO_2 with high-energy, ring-strained heterocyclic molecules, leading to formation of alternating copolymers.[2] The most widely studied one is the alternating copolymerization of CO_2 with epoxides, in the presence of catalysts/cocatalysts.[3,4] The resultant aliphatic polycarbonates possess attractive properties, such as biodegradability and low oxygen permeability, and are regarded as promising new generation materials as alternatives to conventional petrochemical-derived polymers. Consequently, much effort has been devoted toward the development of efficient catalysts for alternating copolymerization of CO_2 with epoxides. Beginning with Inoue's discovery of the $ZnEt_2/H_2O$ catalyst in 1969,[5] a wide array of catalytic systems of metal complexes with various ligands, such as phenoxides,[6] salen and its derivatives,[3a,7] porphyrins,[8] and others,[9] have been explored to promote the transformation. In particular, zinc-β-diketiminate complexes (Chart 1, **A**) developed by Coates[10] have been prominent for the copolymerization of CO_2 with epoxides mainly due to their high catalytic activity and precise control over molecular weight and polydispersity. Furthermore, the system is consistent with a living polymerization process.[10,11]

A number of strategies have been exploited to improve the thermal and mechanical properties of polycarbonates and to expand their applications.[3] These include copolymerization with epoxide momomers other than the commonly applied cyclohexene oxide (CHO) and propylene oxide (PO),[12] terpolymerization with two different epoxides or other types of monomers,[13] and polymer chain cross-linking.[14] Inspired by the success of chiral catalysts in asymmetric organic synthesis, another strategy is to use them to impart control over the absolute and relative stereochemistry of the resulting polycarbonates. The first examples of asymmetric copolymerization of CO_2 and CHO were reported by Nozaki, with a 1:1 mixture of (*S*)-diphenyl(pyrrolidin-2-yl)methanol and $ZnEt_2$ as

Chart 1



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a chiral catalyst,[15] and by Coates, with a series of well-defined, Zn imine-oxazoline catalysts (Chart 1, **B**).[16] The main-chain chirality of the poly(cyclohexene carbonate) (PCHC) was determined to be 70% ee and up to 72% ee, respectively, after hydrolysis to 1,2-*trans*-cyclohexane diol. The former was improved to 80% ee by judicious adjustment of reaction conditions based on mechanistic understandings.[17] Despite its dinuclear nature, Trost's zinc complex was shown to induce rather low enantioselectivity (18% ee) in alternating copolymerization of CO_2 and CHO.[18] Along with the developments of zinc-based catalysts, cobalt and chromium salen complexes were also widely investigated for this asymmetric coupling as well as with *racemic* epoxides.[19] Remarkably, the highest enantioselectivity to date (96% ee) for PCHC was achieved with an unsymmetric enantiopure Co(III)-salen catalyst in combination with a cocatalyst, bis(triphenylphosphine)iminium chloride.[20] Additionally, this approach may serve as a useful method for enantioselective desymmetrization of *meso*-epoxides and kinetic resolution of *racemic* epoxides.

Monoanionic and chelating β-diketiminate ligands have found widespread use in coordination chemistry and catalysis.[21] Modulation of substituents around the ligand skeleton can strongly influence the steric and electronic behavior of the ligands[22] and enables them to be used in numerous catalytic applications.[23] Likewise, isoelectronic and structurally related variants of β-diketiminate ligands, such as triazapentadienates, formazanates, anilido-aldimines, and imine-oxazolinates, have also been examined for different catalytic reactions.[24] Particularly, the anilido-aldimine moiety has been incorporated into dinucleating zinc complexes (Chart 1, **C**) that show high activity toward CO_2/CHO copolymerization.[25] However, the chiral version of these ligands is relatively less explored in catalysis;[26] the Coates's Zn imine-oxazoline catalysts are an eminent example.[16]

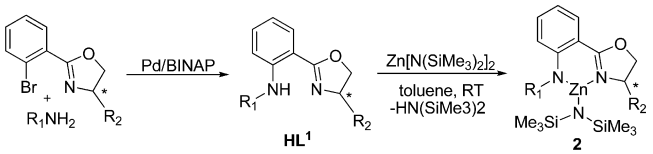
Recently, we have prepared a series of unsymmetrical β-diketimine-type ligands incorporating a chiral 2-oxazoline moiety (Chart 1, **D**).[27] On the basis of the studies mentioned above,[16,25] their zinc complexes are expected to be effective initiators for alternating copolymerization of CO_2 and CHO. Although being C_1 symmetric, they could be advantageous, as the dissymmetric environment is postulated to enhance the asymmetric induction in the CO_2/CHO copolymerization.[20] Herein, we present the synthesis and characterization of zinc complexes of several C_1-symmetric chiral amido-oxazolinate ligands and their catalytic applications in the alternating copolymerization of CO_2 and CHO.

RESULTS AND DISCUSSION

Synthesis of Zinc Complexes. The chiral, unsymmetrical amido-oxazolinate ligands, a variation of β-diketimine type, have been obtained *via* a palladium-catalyzed Buchwald–Hartwig amination reaction (Scheme 1).[27] The modular approach allows independent variations of the two stereo-directing groups (R_1 and R_2) in the ligand framework, and various substituents are incorporated into the framework in order to explore the steric and electronic effects of substituents and their possible synergy in catalysis.

Following previous reports,[10b] the zinc amide complexes (**2a–m**) were prepared by treatment of the free ligands with 1 equiv of $Zn[N(SiMe_3)_2]_2$ in dry toluene at room temperature (Scheme 1).[28] The desired products were readily isolated in high yields within a few hours. In comparison, similar reactions with conventional β-diketiminate ligands were carried out

Scheme 1. Synthesis of Ligands and Zinc Amide Complexes

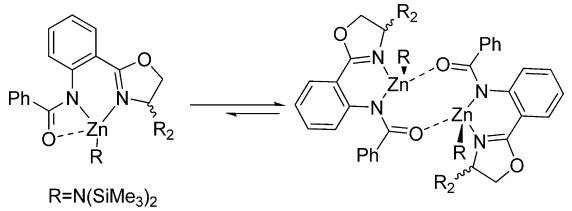


	R1	R2		R1	R2
a	2,6-DMP	(*S*)-^{i}Pr	**g**	2,6-D^{i}PP	(*S*)-^{i}Pr
b	2,6-DMP	(*S*)-^{s}Bu	**h**	2,6-D^{i}PP	(*R*)-^{i}Bu
c	2,6-DMP	(*S*)-^{t}Bu	**i**	(*R*)-CHMePh	(*R*)-^{i}Bu
d	2,6-DMP	(*R*)-^{i}Bu	**j**	(*R*)-CHMeNaph	(*S*)-^{i}Pr
e	2,6-DMP	(*R*)-Ph	**k**	COPh	(*S*)-^{i}Pr
f	3,5-BTP	(*R*)-Ph	**l**	COPh	(*R*)-^{i}Bu
			m	(*S*)-SO^{t}Bu	(*R*)-^{i}Bu

under higher temperature (80 °C) and with longer times (20 h to days).[10b] In the ^{1}H NMR spectra, the disappearance of the free ligand NH signals around 10–11 ppm and the appearance of new broad singlets in the upfield region at 0.1 to −0.05 ppm are consistent with the incorporation of a single amido-oxazolinate ligand in the products. The new broad signals, assigned to the trimethylsilyl groups, usually appear as one singlet at ambient temperature that integrates to 18 protons; however, two broad singlets were observed in some cases for $N(SiMe_3)_2$ protons. The splitting may indicate restricted rotation of the $N(SiMe_3)_2$ group, resulting from its steric interaction with the substituents on either side, e.g., ^{t}Bu (**2c**, **2m**) or D^{i}PP (**2g**, **2h**), or with another $-N(SiMe_3)_2$ group in a dimeric arrangement (**2k**, **2l**). In the ^{13}C NMR spectra, the peaks around 4.80–5.50 ppm were assigned to the carbon of the silyl group, consistent with the formation of the amido-oxazolinate zinc complexes.

Formation of homoleptic bis-ligated zinc complexes was not observed, which may suggest that the steric bulk of the ligands is sufficient to stabilize the unsaturated, three-coordinate metal center and prevent the coordination of an additional ligand. In fact, treatment of complex **2a** with excess THF or pyridine shows no sign of binding, as judged by ^{1}H NMR. However, when the steric bulk is reduced, e.g., in **2k** and **2l**, additional set of signals appears in the ^{1}H NMR spectra. For example, besides the septet at 1.60 ppm, assigned to the methine proton of $-CH(CH_3)_2$ in **2k**, a smaller septet at 1.86 ppm is also observed.[29] This is attributed to the monomer/dimer equilibrium in solution (Scheme 2), which is further supported

Scheme 2. Monomer/Dimer Equilibrium for 2k and 2l



by dilution studies of **2k** using ^{1}H NMR. The relative intensity of the aforementioned signals varies with dilution. As the dilution of the solution was increased, **2k** became a more monomeric species, from which K_{eq} = 75.4 M^{-1} (20 °C in $CDCl_3$) can be derived. The value is analogous to an acetate-bridged β-diketiminate dimer (K_{eq} = 207 M^{-1} at 20 °C in C_6D_6).[10d] Addition of THF or pyridine has little effect on the equilibrium. This may suggest that the side-arm amide oxygen can coordinate intramolecularly or form a bridge between two

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metals. In the solid state, compound **2k** exists as an amide oxygen-bridged dimer, as confirmed by the X-ray structural analysis. However, compound **2m**, with a sulfinamido side arm, shows no evidence of dimer/monomer equilibrium, and a single set of signals is observed in the ^{1}H NMR spectrum. It is possible that **2m** exists as a monomeric species with sulfinamido oxygen weakly coordinated to the zinc center. Given the interest in bimetallic catalysis, the observation here with **2k** and **2l** may suggest a different approach to constructing bimetallic systems.

As zinc β-diketiminate complexes with various initiating groups are known for the copolymerization reaction of epoxides and CO_2, we attempted to synthesize zinc complexes with alkoxide and carboxylate groups, starting from different zinc precursors, such as $Zn(OAc)_2$ and $ZnCl_2$, after deprotonation of ligands with ^{n}BuLi.[10a−d] However, no desired complex was isolated from these reactions. In an alternative route, the zinc amide complex (**2a**) was allowed to react with a stoichiometric amount of 2-propanol, and formation of alkoxide was indicated by the new peaks at 3.42 and 1.60 ppm for ($\mathbf{L}^{1a}$)Zn-O^{i}Pr. However, the reaction appeared to be complicated by side reactions, and attempted purification led to the decomposition of complex to free ligand. These observations are in contrast with the conventional zinc β-diketiminate complexes and may be a reflection of the inherent basicity of the amido nitrogen in the present system.[25]

X-ray Structures. Single crystals of compound **2a** were obtained from concentrated solutions in toluene at −20 °C. The solid-state structure was determined by single-crystal X-ray diffraction techniques; the X-ray crystal data and data collection and refinement parameters are summarized in Table S1 in the Supporting Information. The structure of complex **2a** is depicted in Figure 1 with selected bond distances and bond angles. In agreement with the solution NMR data, **2a** is a monometallic, C_1-symmetric, three-coordinate zinc complex, and the geometry at zinc metal was best described as trigonal planar, as the sum of the bond angles around the zinc atom is 359.48°. The chelating amido-oxazolinate ligand forms a slightly puckered six-membered ring with the zinc metal through its two nitrogen atoms. The bond distance of Zn−N_{imino} (1.968(9) Å) is considerably longer than that of Zn−N_{amido} (1.915(10) Å), presumably due to the stronger interaction with the anionic amido nitrogen. The difference (∼0.05 Å) is similar to those in other unsymmetrical NN bidentate ligation with less resonance character,[30] but longer than those in more symmetrical, β-diketiminate complexes (0.01−0.04 Å).[10b,31] The bond distance of Zn−N3 (1.874(9) Å) is on the shorter end of the Zn−$N_{silylamide}$ bonds reported.[31,32] The bond angle of N1−Zn−N3 (139.15(4)°) is larger than that of N2 −Zn−N3 (125.35(4)°), due to higher steric repulsion between the DMP group and the $N(SiMe_3)_2$ group. This leads to the $N(SiMe_3)_2$ group tilting toward the imine side. On the other hand, due to the chiral center at the 4-oxazoline position (*S* configuration), the plane defined by N3−Si1−Si2 is not perpendicular to the N1−N2−N3 coordination plane; instead, it is twisted 31.43(3)° from its regular perpendicular position, with one of the silyl groups staying away from the ^{i}Pr group on the same side. In turn, the DMP group is 17.66(4)° away from perpendicular to the plane defined by N(1)−N(2)−N(3) due to steric repulsions. Moreover, the bite angle of N1−Zn−N2 was sharper than the other bonds (N1−Zn−N3, N2−Zn−N3).

To further probe the influence of the chiral center on the conformation of the zinc complexes, we determined the X-ray crystal structure of **2d**, containing an *R* configuration at the 4-oxazoline position with a ^{i}Bu group. The modification of the chiral configuration on the oxazoline ring did not lead to considerable changes in the coordination geometry around the metal center. Complex **2d** was isomorphic with **2a**, featuring a distorted trigonal-planar geometry and similar geometric parameters (Figure 2). The smaller bond angle of N2−Zn−N3 = 121.43(7)° in **2d** compared to **2a** (125.35(4)°) can be attributed to the smaller steric bulk of ^{i}Bu (**2d**) compared to ^{i}Pr (**2a**), which imposes less repulsion with the trimethylsilyl group. In accord with this, the six-membered chelating ring is almost planar; the Zn atom is displaced only by 0.0877(2) Å from the plane through other five atoms. Because of the *R* configuration at the chiral center, the silylamido groups twisted

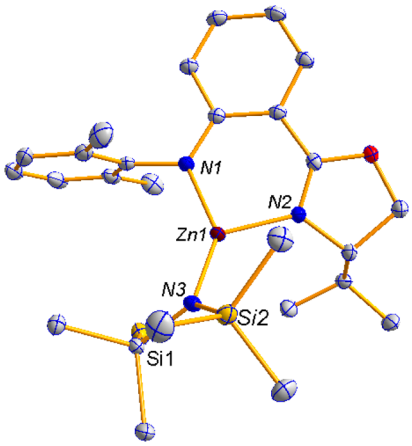

Figure 1. ORTEP drawing of complex **2a** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and bond angles (deg): Zn−N(1) 1.915(10), Zn−N(2) 1.968(9), Zn−N(3) 1.874(9), N(1)−Zn−N(2) 94.98(4), N(1)−Zn−N(3) 139.15(4), N(2)−Zn−N(3) 125.35(4). Hydrogen atoms are omitted for clarity.

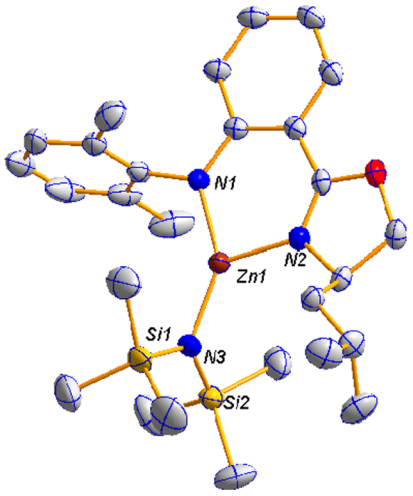

Figure 2. ORTEP drawing of complex **2d** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and bond angles (deg): Zn−N(1) 1.912(15), Zn−N(2) 1.975(16), Zn−N(3) 1.877(15), N(1)−Zn−N(2) 95.84(6), N(1)−Zn−N(3) 142.72(7), N(2)−Zn− N(3) 121.43(7). Hydrogen atoms are omitted for clarity.

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in the opposite orientation (compared with that in **2a**), but to a lesser extent (8.54(7)° vs 31.43(3)° in **2a**), again due to ^{i}Bu being less demanding than ^{i}Pr. The DMP group is slightly tilted, by 12.81(6)°, from its perpendicular position.

Suitable crystals of complex **2k** were obtained from recrystallization in dry toluene at room temperature, and single-crystal X-ray determinations confirm its dimeric form in the solid state (Figure 3). The two zinc centers are bridged by

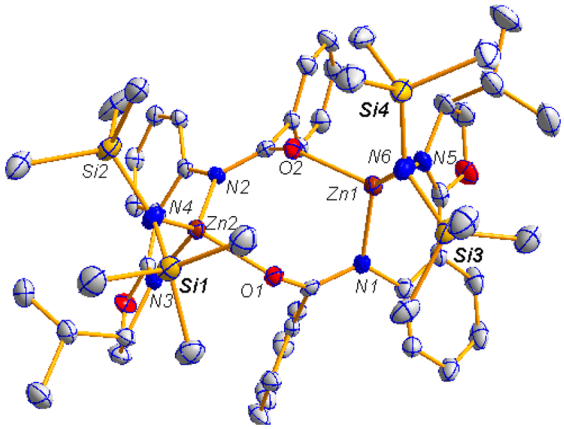

Figure 3. ORTEP drawing of complex **2k** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and bond angles (deg): Zn(1)−N(1) 2.032(2), Zn(1)−N(5) 2.075(2), Zn(1)−N(6) 1.921(19), Zn(1)−O(2) 2.025(16), N(1)−C(1)-1.321(3), O(1)−C(1)1.271(3), N(1) −Zn(1)−N(5) 88.42(8), N(1)−Zn(1)−N(6) 132.52(8), N(5)−Zn(1)−N(6) 115.02(8), N(1)−Zn(1)−O(2) 100.22(7), N(5)−Zn(1)−O(2) 99.32(7). Hydrogen atoms are omitted for clarity.

the amide oxygen of the other ligand to form a tub-like eight-membered ring (Zn1−N1−C1−O1−Zn2−N2−C2−O2). Each zinc metal is ligated with the two nitrogens of the ligand, one nitrogen of the silylamide, and one oxygen atom from benzamide in a distorted tetrahedral geometry. The bond distances of Zn−N are considerally longer than those in monomeric zinc complexes **2a** and **2d**, but are typical of a tetrahedron geometry due to its more crowded environment than the trigonal-planar geometry.[33] The relative distances follow a similar pattern to that in monomeric zinc complexes, as Zn−N_{imino} (2.075(2) Å) is ∼0.043 Å longer than Zn−N_{amido} (2.032(2) Å) and Zn−$N_{silylamide}$ (1.921(19) Å) is the shortest. The two bis(trimethylsilyl)amido groups are oriented in a *syn* fashion. The isopropyl groups on the oxazoline ring and the amido phenyl groups are arranged in an *anti* manner with respect to the NN chelate.

Copolymerization Studies. Our interest in the present system has been twofold. First, we investigate the zinc complexes as potential catalysts for alternating copolymerization of CO_2 and CHO. Second, we want to address the effect of the ligand design on the asymmetric incorporation of CHO monomer into the polymer chain. Compound **2a** was used as a catalyst for initial optimization. Reaction conditions such as temperature, reaction time, pressure of the CO_2, and additive were varied. The selectivity, or the percentage of polycarbonate linkage, was determined by measuring the relative intensity of the methine proton signals of the carbonate linkage (δ = 4.6 ppm) and ether linkage (δ = 3.4 ppm). In no cases was the generation of cyclic carbonate observed (δ = 4.0 ppm). Selected results are listed in Table 1. It is observed that the temperature and CO_2 pressure have a strong influence on the outcome of the copolymerization. The catalyst was inactive at room temperature. As expected, the conversion and carbonate linkages improved with the increasing CO_2 pressure from 100 to 500 psi (entries 2−4). However, further increase in pressure seemed to be detrimental (entry 5). When the initiating group was changed from $N(SiMe_3)_2$ to an alkoxide O^{i}Pr by *in situ* addition of 1 equiv of ^{i}PrOH, comparable results were observed (entry 6 vs 4). Despite the reasonable conversion, only low yields of polycarbonates were isolated, in part due to some weight loss during the reaction (up to 30%). The cause is unclear, but running the reaction without stirring seemed to alleviate the loss, as isolated yields are significantly higher (entry 7), at the expense of longer reaction time and slightly lower carbonate linkage. Raising the temperature to 75 °C increased the conversion and shortened the time to 20 h without sacrificing yield and selectivity (entry 8).

To investigate the effect of ligand architecture on catalytic performance, complexes **2a−m** with systematic modifications in substituents were employed for CHO and CO_2 copolymerization under optimized conditions (500 psi of CO_2 pressure, 75 °C, without stirring, 20 h). The results are summarized in Table 2. Although the reaction rate is slow, with a TOF generally around 3−4 h^{-1}, all the compounds showed appreciable activity, and a white powdery polymer was isolated after workup. It appeared that the conversions were capped at ∼80%, as increased reaction time showed little improvement, probably due to the high viscosity at the end of the reaction.[34] Little or no cyclic carbonate was noted; up to 95% polycarbonate linkage (**2b**) was obtained in the polymers. This level of selectivity is lower than the optimized β-diketiminato zinc

Table 1. Screening of the Conditions for Copolymerization of CO_2 and CHO[a]

entry	temp (°C)	pressure (PSI)	*t*/h	stirring (rpm)	conversion (%)[b]	yield (%)[c]	carbonate linkages (%)[d]
1	RT	100	24	1000	0		
2	50	100	24	1000	42	12	75
3	50	250	24	1000	59	7	85
4	50	500	24	1000	60	15	93
5	50	750	24	1000	27	11	75
6[e]	50	500	24	1000	60	13	96
7[f]	50	500	48	n. s.	62	38	81
8[f]	75	500	20	n. s.	80	36	85

[a]Reaction conditions: Copolymerization reactions were run in neat cyclohexene oxide (CHO) using 1 mol % catalyst **2a**. [b]Determined by ^{1}H NMR spectroscopy on crude reaction mixture. [c]Isolated yield assuming 100% polycarbonates. [d]Calculated by the integration of methine resonances in ^{1}H NMR spectra of polymers. [e]With added ^{i}PrOH (1 equiv to **2a**). [f]Not stirred.

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Table 2. Copolymerization of CHO and CO_2 Using Catalysts 2a−m[a]

entry	cat.	conversion (%)[b]	carbonate linkages (%)[c]	*m*-centered tetrad (%)[d]	yield (%)[e]	M_n (kg/mol)[f]	PDI[f]	*SS*/*RR*[g]
1	**2a**	80	85	69	36	6.5	1.3	42/58
2	**2b**	77	95	67	18	13.4	4.2[h]	*i*
3	**2c**	69	90	69	32	3.1	1.4	48/52
4	**2d**	62	72	66	18	9.1	2.0	56/44
5	**2e**	66	85	62	23	11.6	7.0[h]	52/48
6	**2f**	83	6		42	26.1	1.9	
7	**2g**	82	56	70	32	6.1	1.7	41/59
8	**2h**	81	72	72	43	11.3	1.6	71/29
9	**2i**	58	90	65	20	14.1	7.0[h]	53/47
10	**2j**	59	60	43	13	2.9	1.2	*i*
11	**2k**	78	69	63	17	4.1	1.5	48/52
12	**2l**	81	83	70	16	2.6	1.2	52/48
13	**2m**	18	49	70	4	7.0	1.1	44/56

[a]Copolymerization reactions were carried out in neat CHO at 75 °C with [CHO]:[catalyst] = 100:1 at 500 psi of CO_2. [b]Determined by ^{1}H NMR spectroscopy. [c]Calculated by the integration of methine resonances in ^{1}H NMR spectra of polymers. [d]Determined by ^{13}C NMR spectroscopy. [e]Isolated yields, assuming 100% polycarbonates. [f]Determined by gel permeation chromatography calibrated with polystyrene standards in tetrahydrofuran. [g]Determined by chiral GC on diols after hydrolysis. [h]Bimodel distribution of polymer. [i]Racemic

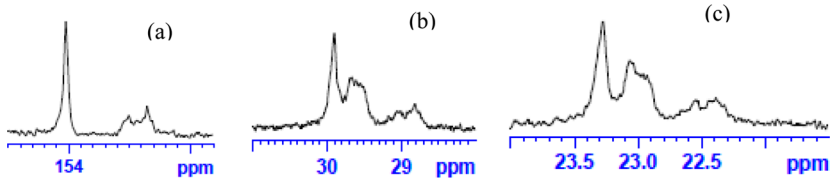

Figure 4. ^{13}C NMR spectrum of the poly(cyclohexene carbonate) generated by catalyst **2c**: (a) carbonyl region; (b and c) methylene region.

catalysts,[10] but is comparable with the more closely related anilido-aldimine zinc catalysts.[25] Electron-withdrawing groups are known to increase the Lewis acidity and catalytic activity of the metal.[10,16] However, introduction of CF_3 groups at the *meta* positions of the phenyl group significantly raised the catalytic activity of **2f** toward homopolymerization of CHO, as only a small amount of polycarbonate linkage (6%) was incorporated, although the molecular weight is high (26.2 kg/mol). Introduction of a second alkyl chiral group at the amido side (**2i**, **2j**) led to lower conversion, presumably because the free rotation of the less bulky substituents on amido nitrogen may hinder CHO entrance to the active site.[4c,10b,35] Restricted rotation of the aniline has been observed to be important in facilitating catalytic activity in olefin polymerization.[36] Despite the less bulky substituent in **2k** and **2l**, both showed high conversion, which may be indicative of bimetallic action. However, compound **2m** with sulfinamide was very sluggish, and it afforded a polymer with high polyether linkage and narrow PDI value.

The molecular weight of the polycarbonate was determined by GPC against a polystyrene standard. The polycarbonate produced by the zinc catalysts showed similar or lower molecular weight compared with calculated values based on conversion, indicative of the presence of a chain transfer process during the reaction, and the molecular weight distribution is somewhat broad (PDI 1.1−2.0). In a few cases (**2b**, **2e**, and **2i**), the PDI values were inflated by the presence of an additional peak at higher molecular weights.[29] The bimodal distributions of polycarbonates have been noted in several zinc-catalyzed copolymerizations and may arise from the presence of multiple active sites or monomer/dimer equilibrium of the catalytic species.[8a,37]

The microstructure (tacticity) of the resulting polymers was characterized by ^{13}C NMR spectroscopy. Typically three distinct resonances were observed at 154.03, 153.52, and 153.37 ppm in the carbonyl regions of PCHCs (Figure 4a). Based on the previous assignments,[16,38] the largest peak at 154.03 ppm was correlated to *m*-centered tetrads ([*mmm*] and [*mmr*]), and the remaining tetrad upfield resonances (δ = 153.52 and 153.37 ppm) were assigned to the *r*-centered tetrads ([*mrm*] and [*mrr*]). The other common tetrads in isotactic polymers [*rmr*] and [*rrr*] were not observed. In accord with this, two series of methylene triad resonances were observed corresponding to two nonequivalent methylene carbons in the ^{13}C NMR spectra (Figure 4b and c). The two downfield resonances (δ = 29.90 (b), 23.28 (c)) correspond to [*mm*] triads, and the intensity is relatively higher than the other triads [*mr*] (δ = 29.66 (b), 23.06 (c)) and [*rr*] (δ = 29.05 (b), 22.54 (c)). The other peaks in this region correspond to polyether linkage.[15,38] On the basis of these assignments, most of the catalysts yield isoenriched PCHC with high *m*-centered tetrads. Increased steric bulk in the catalysts seems to favor higher microstructure regularity in the resultant polycarbonates, as the highest isotacticity (72% *m*-centered tetrads) was obtained with catalyst **2h**, which bears 2,6-D^{i}PP and ^{t}Bu groups on its ligand backbone. Curiously, catalyst **2j** produces a slightly syndioenriched PCHC with 57% *r*-centered tetrads, which is a rather rare case.[38] The two different configurations of chiral centers might have influence on this reverse selectivity.

To further investigate the microstructure assignment and reaction mechanisms, statistical methods were applied to simulate the tetrad distributions observed in PCHC.[16,38] When two models based on chain-end control and enantiomorphic site control mechanisms are compared, the latter seems to give better agreement between calculated and observed tetrad intensities.[29,39] The enantioselectivity parameter α, the probability of an *R* monomer unit adding at the *R* site or an *S* monomer unit adding at the *S* site, has been calculated,

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with the highest value being 0.85 with **2h**.[29] The numbers are comparable with those obtained with zinc imine-oxazoline catalysts.[16] On this basis we hypothesize the present system follows an enantiomorphic site control mechanism.[11,16] However, this process may be competitive with a chain-end control mechanism.[38]

The hydrolysis of resulting copolymers, by an alkali treatment, followed by neutralization with 1 M HCl, gave 1,2-*trans*-cyclohexanediol in 70−80% isolated yields. Chiral GC analysis of the diol indicates that these chiral catalysts can induce asymmetry during the copolymerization, although the enantiomeric excess was generally low (Table 2). Among them, catalyst **2h** exhibited the highest enantiomeric excess of 71:29 (*SS*:*RR*) (Table 2, entry 8). It should be noted that catalyst **2h** also afforded the highest isotacticity in the series. When compared with related zinc imine-oxazoline catalysts (see Chart 1, **B**) with an *RR*:*SS* ratio up to 86:14,[16] the stereoselectivity exhibited by the present catalysts is low, especially considering the resemblance in their structural features and the similarity in the enantioselectivity parameter α. The exact reason is not understood at the moment, although it is suspected that the low selectivity of the present system might be due to some electronic effect resulting from attenuated resonance in the ligand backbone.[40] Nevertheless, they have the same sense of chiral induction, and the chirality of the diol is mostly influenced by the configuration of the oxazoline substituents, as an *R* configuration at the 4-oxazoline position results in enrichment of opposite configurations in the diol unit.[16] The combination of a bulky group at the amide side and a long, bulky group at the imine side seems to work best. The second chiral group at the amide side may also play a significant role; however, a synergistic interaction between the two is not observed.

CONCLUSIONS

A family of new chiral zinc complexes has been synthesized via the reaction of $Zn[N(SiMe_3)_2]_2$ and the corresponding C_1-symmetric, monoanionic amido-oxazolinate ligands (**HL**$^{1a-m}$). While most of them exist as mononuclear complexes, as confirmed by single-crystal X-ray structural analysis of **2a** and **2d**, complexes **2k** and **2l**, with less bulky substituents, are dimeric in the solid state and are in equilibrium between monomer and dimer in solution. All of them are shown to be viable initiators for copolymerization of CO_2 and CHO, yielding polymers with up to 95% polycarbonate linkage and moderate molecular weights and polydispersity values. Modifications around the ligand architecture have a significant influence on the polymerization process. The resultant polymers are isotactic with enriched *m*-centered tetrads, except for **2j**, which produces a syndioenriched PCHC. Induction of main chain chirality is feasible, with up to 42% ee obtained with **2h**, and can be correlated roughly with the chiral centers in ligands, although enantioselectivity is usually very low. In general, catalysts with one chiral center on the oxazoline moiety (R_2 position) and a sufficiently bulky group on the amido nitrogen (R_1 position) seem to provide better structural requirements for activity and selectivity. Current efforts are under way for a better understanding of the effect of ligand architecture in the copolymerization process and improving the activity and selectivity of the catalysts.

EXPERIMENTAL SECTION

General Procedures. All reactions that involved compounds sensitive to air and/or moisture were carried out under a dry nitrogen atmosphere using freshly dried solvents and standard Schlenk line and glovebox techniques. All chemicals were purchased from Aldrich except where noted. Toluene was distilled under nitrogen from Na/benzophenone. $CDCl_3$ and C_6D_6 were dried over CaH_2 and Na/benzophenone, respectively, and distilled and degassed prior to use. Carbon dioxide (Airgas, high purity, 99.995%) was used as received. Cyclohexene oxide was distilled from CaH_2 following three freeze−pump−thaw cycles and stored in a glovebox prior to use. Zinc bis(trimethylsilyl)amide was prepared according to the literature.[41]

NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer (^{1}H and ^{13}C). Chiral GC analysis was carried out on an Agilent 7890 with FID detector using a chiral column (cyclodex-B, 30 m × 0.250 mm × 0.25 μm). The temperature program was as follows: injector temperature 250 °C, detector 300 °C, oven initial temperature 120 °C, hold for 30 min, ramp at 30 °C/min to 200 °C, hold for 10 min. Inlet flow: 85 mL/min (split mode, 68:1). Gel permeation chromatography (GPC) analysis was performed on a Varian Prostar, using a PLgel 5 μm Mixed-D column, a Prostar 355 RI detector, and THF as eluent at a flow rate of 1 mL/min (20 °C). Polystyrene standards were used for calibration.

*Synthesis of (4S)-4,5-Dihydro-2-[2′-(2,6-dimethylanilino)phenyl]-4-tert-butyloxazole (**HL**^{1c}).* Synthesis of this new ligand was performed analogously following the literature.[27] Yield: 98%. ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): 0.95 (9H, s, C(CH_3)$_3$), 2.22 (6H, s, Ar*Me*), 4.27 (2H, m, NCH(R)CH_2O), 4.30 (1H, m, NC*H*(R)-CH_2O), 6.23 (1H, d, *J* = 8.80, *m*-Ph*H*N), 6.65 (1H, t, *J* = 7.50, *p*-Ph*H*(CH_3)$_2$), 7.10−7.15 (4H, br, Ar*H*), 7.79 (1H, d, *J* = 7.90, *o*-Ph*H*N), 10.01 (1H, br, N*H*). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 18.62 (Ar*Me*), 26.07 (C(*C*H$_3$)$_3$), 34.10 (*C*(CH$_3$)$_3$), 67.02 (NCH(R)-CH_2O), 76.42 (NCH(R)CH_2O), 108.66, 112.72, 115.35, 126.22, 129.90, 132.29 (CH_{arom}), 136.47, 137.03, 138.23, 147.84, 164.05 (C_{quart}). GC/MS: *m*/*z* 322[M]$^+$, 307, 291, 222, 208, 194. HRMS (ESI): *m*/*z* calcd for $C_{21}H_{26}N_2O$ [M]$^+$ 322.20451; found 322.21233.

*Synthesis of (4R)-4,5-Dihydro-2-[2′-(3,5-bis(trifluoromethyl)-anilino)phenyl]-4-phenyloxazole (**HL**^{1f}).* Synthesis of this new ligand was performed analogously following the literature.[27] Yield: 66%. ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): 3.84 (1H, t, *J* = 8.12, NC*H*(R)CH$_2$O), 4.39 (1H, t, *J* = 8.80, NCH(R)CH_2O), 5.51 (1H, m, t, *J* = 8.70, NCH(R)CH_2O), 6.46 (1H, d, *J* = 7.8 *m*-Ph*H*N), 6.96 (3H, m, Ar*H*), 7.02−7.04 (4H, m, Ar*H*), 7.05−7.09 (3H, m, Ar*H*), 7.60 (1H, dr, *J* = 8.2, *o*-Ph*H*N), 10.51 (1H, br, N*H*). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 70.32 (NCH(R)CH$_2$O), 73.62 (NCH(R)-CH$_2$O), 112.27 (Ar-CF$_3$), 114.35 (Ar-CF$_3$), 115.29, 119.67, 119.80, 120.01, 122.44, 124.60, 126.70, 128.02, 129.07, 130.78 (CH_{arom}) 132.20, 132.77, 133.27, 142.31, 143.60, 143.98, 163.40 (C_{quart}). GC/MS: *m*/*z* 450[M]$^+$, 331, 331, 304. HRMS (ESI): *m*/*z* calcd for $C_{23}H_{17}F_6N_2O$ [M + H]$^+$ 451.12451; found 451.12450.

*Synthesis of [(**L**^{1a})ZnN(SiMe$_3$)$_2$] (**2a**).* A solution of ligand **HL**^{1a} (414 mg, 1.342 mmol) in toluene (10 mL) was added into zinc bis(trimethylsilyl)amide (543 mg, 1.406 mmol) in toluene (5 mL) at room temperature. After being stirred for 8 h, the pale yellow solution was dried *in vacuo*, giving the desired compound as a yellow powder (98%, 704 mg). Recrystallization from toluene at −20 °C gave yellow-colored crystals (90%, 643 mg) suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.15 (18H, s, N(SiMe$_3$)$_2$), 0.90 (3H, d, *J* = 7.14, (CH_3)$_2$CH), 1.02 (3H, d, *J* = 7.10, (CH_3)$_2$CH), 2.01 (3H, s, Ar*Me*), 2.24 (3H, s, Ar*Me*), 2.41 (1H, m, (CH$_3$)$_2$C*H*), 4.39 (1H, t, *J* = 7.10, NC*H*(R)CH$_2$O), 4.47 (1H, t, *J* = 8.0, NCH(R)CH_2O), 4.51 (1H, m, NCH(R)CH_2O), 6.22 (1H, d, *J* =8.70, *m*-Ph*H*N), 6.45 (1H, t, *J* = 8.10, *p*-Ph*H*(CH$_3$)$_2$), 7.01 (1H, t, *J* = 7.94, *m*-Ph*H*N), 7.08 (2H, br, *m*-Ph*H*(CH$_3$)$_2$), 7.16 (1H, t, *J* = 7.84, *p*-Ph*H*N), 7.82 (1H, d, *J* = 8.06 *o*-Ph*H*N). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 4.87 (Si*Me*$_3$), 15.10 ((CH)*Me*$_2$), 19.10 (Ar*Me*), 19.16 (Ar*Me*), 31.38 ((CH)Me$_2$), 66.94 (NCH(R)CH$_2$O), 69.24 (NCH-(R)CH_2O), 103.86, 113.05, 116.24, 124.41, 129.99, 131.60 (CH_{arom}), 134.25, 134.51, 147.2, 157.18, 169.50 (C_{quart}). Anal. Calcd for

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$C_{26}H_{41}N_3OSi_2Zn$: C, 58.57; H, 7.75; N, 7.88. Found: C, 57.18; H, 7.91; N, 7.58.

*Synthesis of [(L^{1b})ZnN(SiMe$_3$)$_2$] (**2b**).* A solution of ligand **HL^{1b}** (237 mg, 0.735 mmol) in toluene (5 mL) was added into zinc bis(trimethylsilyl)amide (283 mg, 0.735 mmol) in toluene (5 mL) at room temperature. After being stirred for 8 h, the pale yellow colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (89%, 357 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.24 (18H, s, CH_3), 0.84 (3H, m, $CH_3CHCH_2CH_3$), 1.02 (3H, m, $CH_3CHCH_2CH_3$), 1.27 (1H, m, CH_3CHCH_2 CH_3), 1.34 (1H, m, $CH_3CHCH_2CH_3$), 1.43 (1H, m, $CH_3CHCH_2CH_3$), 2.00 (3H, s, ArMe), 2.18 (3H, s, ArMe), 4.49 (1H, t, J = 8.54, NCH(R)CH_2O), 4.55 (1H, t, J = 9.67, NCH(R)CH_2O), 4.61 (1H, t, J = 8.55, NCH(R)CH_2O), 6.23 (1H, d, J = 9.30, *m*-PhHN), 6.47 (1H, t, J = 7.90, *p*-Ph$H(CH_3)_2$), 7.01 (1H, t, J = 7.67, *p*-PhHN), 7.07 (1H, br, *m*-PhHN), 7.23−7.48 (2H, br, *m*-Ph$H(CH_3)_2$), 7.81 (1H, d, J = 8.29, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 4.80 ($SiMe_3$), 12.10 ($CHCH_2(CH_3)_2$), 12.21 ($CHCH_2(CH_3)_2$), 18.69 (ArMe), 18.98 (ArMe), 26.85 ($CHCH_2(CH_3)_2$), 37.98 ($CHCH_2(CH_3)_2$), 66.61 (NCH(R)CH_2O), 68.17 (NCH(R)CH_2O), 103.96, 113.03, 116.25, 124.36, 125.53, 128.47 (CH_{arom}), 131.02, 131.20, 134.41, 147.22, 157.11, 169.45 (C_{quart}). Anal. Calcd for $C_{27}H_{43}N_3OSi_2Zn{\cdot}0.2C_7H_8$: C, 60.30; H, 7.95; N, 7.43. Found: C, 60.39; H, 7.61; N, 6.67.

*Synthesis of [(L^{1c})ZnN(SiMe$_3$)$_2$] (**2c**).* To a solution of ligand **HL^{1c}** (113 mg, 0.350 mmol) in toluene (5 mL) was added zinc bis(trimethylsilyl)amide (135 mg, 0.351 mmol) at room temperature. After being stirred for 8 h, ^{1}H NMR confirmed the incomplete conversion of the ligand into a zinc complex. An additional amount of zinc bis(trimethylsilyl)amide (8 mg, 0.021 mmol) was added. After 4 h of stirring, the yellow-colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (92%, 177 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.36 (9H, s, CH_3), 0.04 (9H, s, CH_3), 1.01 (9H, s, $C(CH_3)_3$), 2.23 (3H, s, ArMe), 2.27 (3H, s, ArMe), 4.21 (1H, m, NCH(R)CH_2O), 4.40 (1H, t, J = 9.70, NCH(R)CH_2O), 4.56 (1H, m, NCH(R)CH_2O), 6.20 (1H, d, J = 9.13, *m*-PhHN), 6.42 (1H, m, *p*-Ph$H(CH_3)_2$), 7.02−7.18 (3H, m, ArH), 7.20 (1H, m, ArH), 7.83 (1H, d, J = 8.28, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 5.19 ($SiMe_3$), 5.28 ($SiMe_3$), 18.46 (ArMe), 18.84 (ArMe), 25.27 ($C(CH_3)_3$), 34.95 ($C(CH_3)_3$), 68.41 (NCH(R)CH_2O), 73.34 (NCH(R)CH_2O), 103.37, 112.85, 115.82, 124.50, 128.99, 129.28, 131.81 (CH_{arom}), 134.20, 134.62, 134.78, 147.09, 157.37, 170.54 (C_{quart}).

*Synthesis of [(L^{1d})ZnN(SiMe$_3$)$_2$] (**2d**).* A solution of ligand **HL^{1d}** (316 mg, 0.980 mmol) in toluene (10 mL) was added into zinc bis(trimethylsilyl)amide (378 mg, 0.980 mmol) in toluene (5 mL) at room temperature. After being stirred for 8 h, the pale yellow colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (552 mg). The light yellow colored solid was recrystallized from toluene at −20 °C to give yellow-colored crystals (93%, 502 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.01 (18H, s, CH_3), 1.21 (6H, m, $CH_2CH(CH_3)_2$), 1.74 (1H, m, $CH_2CH(CH_3)_2$), 1.93 (1H, m, $CH_2CH(CH_3)_2$), 2.22 (3H, s, ArMe), 2.39 (3H, s, ArMe), 2.45 (1H, m, $CH_2CH(CH_3)_2$), 4.39 (1H, t, J = 8.23, NCH(R)CH_2O), 4.74 (1H, m, NCH(R)CH_2O), 4.84 (1H, t, J = 8.90, NCH(R)CH_2O), 6.42 (1H, d, J = 8.90, *m*-PhHN), 6.63 (1H, m, *p*-Ph$H(CH_3)_2$, 7.19 (1H, br, *p*-PhHN), 7.33 (2H, m, *m*-Ph$H(CH_3)_2$), 7.45 (1H, m, *m*-Ph$H(CH_3)_2$), 8.03 (1H, d, J = 8.50, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 5.04 ($SiMe_3$), 18.71 ($CHCH_2(CH_3)_2$), 19.07 ($CHCH_2(CH_3)_2$), 22.23 ($CHCH_2(CH_3)_2$), 23.96 (ArMe), 25.83 (ArMe), 45.68 ($CH_2CH(CH_3)_2$), 63.60 (NCH(R)CH_2O), 71.80 (NCH(R)CH_2O), 104.03, 113.10, 116.26, 124.39, 125.47, 128.56, 129.03 (CH_{arom}), 134.04, 134.17, 134.47, 147.27, 157.05, 169.50 (C_{quart}). Anal. Calcd for $C_{27}H_{43}N_3OSi_2Zn$: C, 59.26; H, 7.92; N, 7.68. Found: C, 59.04; H, 7.84; N, 7.44.

*Synthesis of [(L^{1e})ZnN(SiMe$_3$)$_2$] (**2e**).* To a solution of the ligand **HL^{1e}** (265 mg, 0.774 mmol) in toluene (10 mL) was added zinc bis(trimethylsilyl)amide (301 mg, 0.780 mmol) at room temperature. After being stirred for 8 h, the pale yellow colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (96%, 421 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.35 (18H, s, $N(SiMe_3)_2$), 1.98 (3H, s, ArMe), 2.23 (3H, s, ArMe), 4.53 (1H, m, NCH(R)CH_2O), 4.90 (1H, t, J = 8.90, NCH(R)CH_2O), 5.53 (1H, m, NCH(R)CH_2O), 6.27 (1H, d, J = 8.85, *m*-PhHN), 6.50 (1H, t, J = 7.57, *p*-Ph$H(CH_3)_2$), 6.99 (1H, t, J = 7.81, *p*-PhHN), 7.06 (1H, m, *m*-PhHN), 7.12 (2H, m, *m*-Ph$H(CH_3)_2$), 7.35−7.40 (5H, m, C_3H_3NOPhH), 7.93 (1H, d, J = 8.37, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 4.87 ($SiMe_3$), 18.67 (ArMe), 18.98 (ArMe), 68.11 (NCH(R)CH_2O), 74.0 (NCH(R)CH_2O), 103.86, 116.40, 118.24, 121.33, 124.39, 125.54, 127.09, 128.46, 128.92, 129.27, 129.50, 131.67 (CH_{arom}), 134.00, 134.09, 134.70, 141.34, 147.10, 157.46, 170.19 (C_{quart}). Anal. Calcd for $C_{29}H_{39}N_3OSi_2Zn{\cdot}0.5CH_2Cl_2$: C, 58.11; H, 6.61; N, 6.89. Found: C, 58.25; H, 6.79; N, 6.43.

*Synthesis of [(L^{1f})ZnN(SiMe$_3$)$_2$] (**2f**).* To a solution of ligand **HL^{1f}** (79 mg, 0.175 mmol) in toluene (4 mL), was added zinc bis(trimethylsilyl)amide (68 mg, 0.175 mmol) at room temperature. After being stirred for 8 h, the pale yellow colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (68%, 82 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.32 (18H, s, CH_3), 4.56 (1H, m, NCH(R)CH_2O), 4.93 (1H, t, J = 7.80, NCH(R)CH_2O), 5.51 (1H, m, NCH(R)CH_2O), 6.46 (2H, m, ArH), 7.06 (1H, m, ArH), 7.19 (2H, m, ArH), 7.33−7.44 (3H, m, ArH), 7.53 (2H, m, ArH), 7.58 (1H, br, ArH), 8.02 (1H, d, J = 9.35, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$): 5.52 ($SiMe_3$), 68.45 (NCH(R)CH_2O), 74.39 (NCH(R)CH_2O),115.30 (CF_3), 117.50 (CF_3), 122.50, 124.70, 125.55, 126.84, 127.33, 128.47, 128.62, 129.30, 129.74, 132.14 (CH_{arom}), 133.14, 135.22, 140.41, 152.67, 156.69, 157.38, 170.50 (C_{quart}).

*Synthesis of [(L^{1g})ZnN(SiMe$_3$)$_2$] (**2g**).* To a solution of ligand **HL^{1g}** (400 mg, 1.097 mmol) in toluene (15 mL) was added zinc bis(trimethylsilyl)amide (424 mg, 1.098 mmol) at room temperature. After being stirred for 8 h, the yellow-colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (89%, 575 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.30 (9H, s, CH_3), 0.03 (9H, s, CH_3), 0.92 (3H, d, J = 6.81, $CH(CH_3)_2$), 1.07 (6H, d, J = 7.03, $ArCH(CH_3)_2$), 1.17 (3H, d, J = 6.91, $CH(CH_3)_2$), 1.29 (6H, d, J = 6.75, $ArCH(CH_3)_2$), 1.57 (1H, m, $CH(CH_3)_2$), 3.02 (1H, m, $ArCH(CH_3)_2$), 3.28 (1H, m, $ArCH(CH_3)_2$), 4.40 (1H, t, J = 7.75, NCH(R)CH_2O), 4.47 (1H, t, J = 8.49, NCH(R)CH_2O), 4.54 (1H, m, NCH(R)CH_2O), 6.25 (1H, d, J = 9.25, *m*-PhHN), 6.44 (1H, t, J = 8.49, *p*-Ph$H(CH_3)_2$), 7.19 (1H, t, J = 7.13, *m*-PhHN), 7.20−7.24 (3H, m, ArH), 7.81 (1H, d, J = 8.41, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 5.10 ($SiMe_3$), 5.19 ($SiMe_3$), 21.20 ($CH(CH_3)_2$), 22.40 ($CH(CH_3)_2$), 24.25 ($CH(CH_3)_2$), 25.68 ($ArCH(CH_3)_2$), 26.54 ($ArCH(CH_3)_2$), 27.92 ($ArCH(CH_3)_2$), 28.92 ($ArCH(CH_3)_2$), 39.25 ($ArCH(CH_3)_2$), 41.01 ($ArCH(CH_3)_2$), 63.01 (NCH(R)CH_2O), 73.55 (NCH(R)CH_2O), 105.05, 112.12, 116.60, 122.26, 124.53, 127.46, 128.27 (CH_{arom}), 132.42, 136.49, 138.48, 144.89, 155.88, 168.54 (C_{quart}).

*Synthesis of [(L^{1h})ZnN(SiMe$_3$)$_2$] (**2h**).* To a solution of ligand **HL^{1h}** (137 mg, 0.362 mmol) in toluene (6 mL) was added zinc bis(trimethylsilyl)amide (140 mg, 0.362 mmol) at room temperature, and the mixture was stirred for 8 h. The pale yellow colored solution was dried *in vacuo*, to give a yellow compound (89%, 195 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.22 (9H, s, CH_3), 0.03 (9H, s, CH_3), 0.92 (3H, d, J = 6.81, $CH_2CH(CH_3)_2$), 1.07 (6H, d, J = 7.03, $ArCH(CH_3)_2$), 1.17 (3H, d, J = 6.91, $CH_2CH(CH_3)_2$), 1.29 (6H, d, J = 6.75, $ArCH(CH_3)_2$), 1.57 (1H, m, $CH_2CH(CH_3)_2$), 1.76 (1H, m, $CH_2CH(CH_3)_2$), 2.22 (1H, m, $CH_2CH(CH_3)_2$), 3.07 (1H, m, $ArCH(CH_3)_2$), 3.28 (1H, m, $ArCH(CH_3)_2$), 4.26 (1H, t, J = 7.75, NCH(R)CH_2O), 4.60 (1H, m, NCH(R)CH_2O), 4.66 (1H, t, J = 8.49, NCH(R)CH_2O), 6.26 (1H, d, J = 9.25, *m*-PhHN), 6.44 (1H, t, J = 8.49, *p*-Ph$H(CH_3)_2$), 7.05 (1H, t, J = 7.13, *m*-PhHN), 7.20−7.28 (3H, m, ArH), 7.83 (1H, d, J = 8.41, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 5.21 ($SiMe_3$), 5.30 ($SiMe_3$), 22.30 ($CHCH_2(CH_3)_2$), 23.86 ($CHCH_2(CH_3)_2$), 24.25 ($CHCH_2(CH_3)_2$), 24.55 ($CHCH_2(CH_3)_2$), 25.33 ($ArCH(CH_3)_2$), 25.54 ($ArCH(CH_3)_2$), 25.92 ($ArCH(CH_3)_2$), 25.92 ($ArCH(CH_3)_2$), 28.25 ($ArCH(CH_3)_2$), 45.01 ($ArCH(CH_3)_2$), 63.61 (NCH(R)CH_2O), 71.55 (NCH(R)-CH_2O), 104.05, 113.12, 118.60, 124.26, 125.53, 128.46, 131.25 (CH_{arom}), 133.61, 138.10, 144.61, 144.90, 158.59, 169.50 (C_{quart}).

*Synthesis of [(L^{1i})ZnN(SiMe$_3$)$_2$] (**2i**).* To a solution of ligand **HL^{1i}** (56 mg, 0.173 mmol) in toluene (10 mL) was added zinc

bis(trimethylsilyl)amide (67 mg, 0.173 mmol) at room temperature, and the mixture was stirred for 8 h. The pale yellow colored solution was dried *in vacuo*, to afford the desired compound as a yellow powder (68%, 65 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): 0.21 (18H, s, CH_3), 1.12 (6H, m, $CH_2CH(CH_3)_2$), 1.32 (1H, m, $CH_2CH(CH_3)_2$), 1.56 (1H, m, $CH_2CH(CH_3)_2$), 1.74 (1H, m, $CH_2CH(CH_3)_2$), 2.22 (3H, d, J = 8.35, $ArCHCH_3$), 4.18 (1H, m, $ArCHCH_3$), 4.58 (2H, m, $NCH(R)CH_2O$), 5.05 (1H, m, $NCH(R)CH_2O$), 6.50 (1H, t, J = 9.35, *m*-PhHN), 6.83 (1H, d, J = 9.35, *m*-PhHN), 7.12 (2H, t, J = 8.13, *o*-PhH), 7.20−7.28 (4H, m, ArH), 7.97 (1H, d, J = 6.45, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 5.52 ($SiMe_3$), 21.68 ($CHCH_2(CH_3)_2$), 24.14 ($CHCH_2(CH_3)_2$), 26.25 ($ArCHCH_3$), 44.68 ($CHCH_2(CH_3)_2$), 58.08 ($ArCHCH_3$), 63.85 ($NCH(R)CH_2O$), 71.20 ($NCH(R)CH_2O$), 104.97, 112.56, 116.92, 126.34, 128.44, 128.62, 129.87, 131.85, 134.26 (CH_{arom}), 147.21, 158.03, 169.51 (C_{quart}). Anal. Calcd for $C_{27}H_{43}N_3OSi_2Zn$: C, 59.26; H, 7.92; N, 7.68. Found: C, 59.35; H, 7.68; N, 7.73.

*Synthesis of [(L^{1j})ZnN(SiMe$_3$)$_2$] (**2j**).* To a solution of ligand **HL^{1j}** (283 mg, 0.790 mmol) in toluene (10 mL) was added zinc bis(trimethylsilyl)amide (305 mg, 0.790 mmol) at room temperature. After being stirred for 8 h, the pale yellow colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (88%, 405 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): 0.04 (18H, s, CH_3), 0.89 (3H, d, J = 7.60, $CH(CH_3)_2$), 1.04 (3H, d, J = 8.01, $CH(CH_3)_2$), 1.98 (3H, d, J = 8.22, $ArCHCH_3$), 2.67 (1H, m, $CH(CH_3)_2$), 4.42 (2H, m, $NCH(R)CH_2O$), 4.61 (1H, m, $NCH(R)CH_2O$), 5.50 (1H, br, $C_{12}H_{11}$), 6.40 (1H, t, J = 7.80, *p*-PhHN), 6.45 (1H, d, J = 9.35, *m*-PhHN), 6.97 (1H, t, J = 7.80, *m*-PhHN), 7.20 (1H, d, J = 7.80, ArH), 7.33 (1H, t, J = 9.35, ArH), 7.55 (1H, m, ArH), 7.61 (1H, t, J = 9.35, ArH), 7.71 (1H, d, J = 9.35, *o*-PhHN), 7.85 (1H, d, J = 9.35, ArH), 7.92 (1H, d, J = 9.35, ArH), 8.25 (1H, d, J = 9.35, ArH). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 5.50 ($SiMe_3$), 14.35 ($CH(CH_3)_2$), 19.37 ($CH(CH_3)_2$), 28.31 ($ArCHCH_3$), 30.44 ($CH(CH_3)_2$), 55.50 ($ArCH(CH_3)$), 66.13 ($NCH(R)CH_2O$), 69.27 ($NCH(R)CH_2O$), 105.20, 112.70, 117.22, 121.78, 123.06, 125.52, 126.13, 127.0, 128.40, 129.30, 131.04 (CH_{arom}), 134.43, 142.20, 147.95, 159.62, 160.73, 169.53 (C_{quart}). Anal. Calcd for $C_{30}H_{43}N_3OSi_2Zn{\cdot}0.2C_7H_8$: C, 62.68; H, 7.47; N, 6.98. Found: C, 62.59; H, 7.25; N, 6.32.

*Synthesis of [(L^{1k})ZnN(SiMe$_3$)$_2$] (**2k**).* To a solution of ligand **HL^{1k}** (333 mg, 1.081 mmol) in toluene (6 mL) was added zinc bis(trimethylsilyl)amide (418 mg, 1.082 mmol) at room temperature. After being stirred for 8 h, the pale yellow colored solution was dried *in vacuo*, and the residue was recrystallized from toluene at −30 °C to afford **2k** (84%, 483 mg) as light pinkish crystals. ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K; peaks for the minor species are only partially identified due to overlap): Major: 0.06 (9H, s, CH_3), 0.09 (9H, s, CH_3), 0.64 (3H, d, J = 7.12,$CH(CH_3)_2$), 0.68 (3H, d, J = 7.12,$CH(CH_3)_2$), 1.60 (1H, m, $CH(CH_3)_2$), 4.09 (1H, m, $NCH(R)CH_2O$), 4.28 (1H, t, J = 7.91, $NCH(R)CH_2O$), 4.35 (1H, t, J = 7.09, $NCH(R)CH_2O$), 6.87 (1H, d, J = 9.210, *m*-PhHN), 7.10 (4H, m, ArH), 7.20−7.25 (6H, m, ArH), 7.45 (2H, d, J = 9.41, COPh-*H*), 7.73 (1H, d, J = 9.41, *o*-PhHN). Minor: 0.59 (3H, d, J = 7.09, $CH(CH_3)_2$), 0.84 (3H, d, J = 7.06, $CH(CH_3)_2$), 1.86 (1H, m, $CH(CH_3)_2$), 6.96 (1H, t, J = 9.49, *m*-PhHN), 7.62 (2H, d, J = 8.81, COPh-*H*), 7.69 (1H, d, J = 9.50, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): Major: 5.95 ($SiMe_3$), 14.86 ($(CH)Me_2$), 18.93 ($(CH)Me_2$), 30.24 ($(CH)Me_2$), 67.56 ($NCH(R)CH_2O$), 69.61 ($NCH(R)CH_2O$), 121.32, 127.32, 128.28, 128.43, 129.22, 129.66, 130.66, 133.56, 138.05 (CH_{arom}), 140.77, 151.41, 168.82, 176.34 (C_{quart}). Minor: 5.69 ($SiMe_3$), 15.58 ($(CH)Me_2$), 19.26 ($(CH)Me_2$), 31.13 ($(CH)Me_2$), 68.03 ($NCH(R)CH_2O$), 69.98 ($NCH(R)CH_2O$), 120.31, 127.63, 127.90, 128.53, 128.79, 129.06, 130.06, 132.98, 137.45 (CH_{arom}), 139.58, 150.87, 168.40, 176.14 (C_{quart}). Anal. Calcd for $C_{50}H_{74}N_6O_4Si_4Zn_2{\cdot}0.4C_7H_8$: C, 57.49; H, 7.05; N, 7.62. Found: C, 57.88; H, 6.56; N, 7.65.

*Synthesis of [(L^{1l})ZnN(SiMe$_3$)$_2$] (**2l**).* To a solution of ligand **HL^{1l}** (68 mg, 0.211 mmol) in toluene (6 mL) was added zinc bis(trimethylsilyl)amide (84 mg, 0.211 mmol) at room temperature. After being stirred for 8 h, the pale yellow colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (98%, 113 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K; peaks for the minor species are only partially identified due to overlap): Major: −0.04 (9H, s, CH_3), 0.08 (9H, s, CH_3), 0.62 (3H, d, J = 7.15, $CH_2CH(CH_3)_2$), 0.97 (3H, d, J = 6.80, $CH_2CH(CH_3)_2$), 1.27 (1H, m, $CH_2CH(CH_3)_2$), 1.50 (1H, m, $CH_2CH(CH_3)_2$), 1.73 (1H, m, $CH_2CH(CH_3)_2$), 3.75 (1H, t, J = 9.10, $NCH(R)CH_2O$), 4.50 (2H, t, J = 8.90, $NCH(R)CH_2O$), 6.84 (2H, m, ArH), 7.04 (2H, m, ArH), 7.16 (1H, m, ArH), 7.52 (1H, m, ArH), 7.63 (2H, m, ArH), 7.91 (1H, d, J = 8.10, *o*-PhHN). Minor: 0.52 (3H, d, J = 6.50, $CH_2CH(CH_3)_2$), 1.04 (3H, d, J = 6.80, $CH_2CH(CH_3)_2$), 1.24 (1H, m, $CH_2CH(CH_3)_2$), 1.44 (1H, m, $CH_2CH(CH_3)_2$), 1.93 (1H, m, $CH_2CH(CH_3)_2$), 4.00 (1H, m, $NCH(R)CH_2O$), 4.14 (1H, m, $NCH(R)CH_2O$), 4.22 (1H, m, $NCH(R)CH_2O$), 6.94 (2H, m, ArH), 7.36 (1H, m, ArH), 8.11 (1H, d, J = 7.50, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): Major: 5.85 ($SiMe_3$), 21.12 ($CHCH_2(CH_3)_2$), 22.36 ($CHCH_2(CH_3)_2$), 24.01 ($CHCH_2(CH_3)_2$), 25.02 ($CHCH_2(CH_3)_2$), 67.61 ($NCH(R)CH_2O$), 74.55 ($NCH(R)CH_2O$), 104.05, 113.12, 119.60, 124.26, 125.53, 128.46, 133.61, 138.10, 145.49 (CH_{arom}), 158.19, 165.09, 169.50, 176.18 (C_{quart}). Minor: 5.01 ($SiMe_3$), 20.01 ($CHCH_2(CH_3)_2$), 23.01 ($CHCH_2(CH_3)_2$), 24.18 ($CHCH_2(CH_3)_2$), 26.12 ($CHCH_2(CH_3)_2$), 69.76 ($NCH(R)CH_2O$), 77.85 ($NCH(R)CH_2O$), 104.35, 113.32, 119.01, 124.89, 126.01, 129.06, 133.89, 139.08, 145.01(CH_{arom}), 158.59, 165.89, 170.04, 176.30 (C_{quart}).

*Synthesis of [(L^{13-}) ZnN(SiMe$_3$)$_2$] (**2m**).* To a solution of ligand **HL^{1m}** (364 mg, 1.129 mmol) in toluene (15 mL) was added zinc bis(trimethylsilyl)amide (436 mg, 1.129 mmol) at room temperature. After being stirred for 8 h, the pale red colored solution was dried *in vacuo*, giving the desired compound as a yellow powder (86%, 531 mg). ^{1}H NMR (500.1 MHz; $CDCl_3$; 298 K): −0.28 (9H, s, CH_3), 0.07 (9H, s, CH_3), 0.92 (6H, br, $CH_2CH(CH_3)_2$), 1.11 (2H, m, $CH_2CH(CH_3)_2$), 1.31 (1H, m, $CH_2CH(CH_3)_2$), 1.54 (9H, s, $C(CH_3)_3$), 2.81 (1H, t, J = 8.83, $NCH(R)CH_2O$), 3.69 (1H, t, J = 6.91, $NCH(R)CH_2O$), 4.06 (1H, t, J = 8.49, $NCH(R)CH_2O$), 6.86 (1H, t, J = 7.63, *p*-PhHN), 7.04 (1H, d, J = 8.23, *m*-PhHN), 7.32 (1H, t, J = 7.93, *m*-PhHN), 7.69 (1H, d, J = 7.93, *o*-PhHN). ^{13}C NMR (125.8 MHz; $CDCl_3$; 298 K): 5.20 ($SiMe_3$), 5.75 ($SiMe_3$), 21.28 ($CHCH_2(CH_3)_2$), 23.68 ($CHCH_2(CH_3)_2$), 25.08 ($CHCH_2(CH_3)_2$), 25.93 ($C(CH_3)_3$), 43.17 ($CHCH_2(CH_3)_2$), 59.56 ($C(CH_3)_3$), 65.30 ($NCH(R)CH_2O$),70.51 ($NCH(R)CH_2O$), 115.72, 119.02, 123.49, 131.09 (CH_{arom}), 145.95, 154.52, 165.72 (C_{quart}). Anal. Calcd for $C_{23}H_{43}N_3O_2SSi_2Zn{\cdot}0.3C_7H_8$: C, 52.51; H, 7.99; N, 7.29. Found: C, 52.69; H, 7.66; N, 7.32.

Copolymerization of Cyclohexene Oxide/CO_2. In a glovebox, a 60 mL Teflon-lined Parr high-pressure reactor vessel that was previously dried in an oven was charged with a zinc catalyst (1 mol %) and CHO (1 equiv). The vessel was sealed, taken out of the glovebox, and brought to desired temperature and CO_2 pressure. After the mixture was stirred for the allotted time, it was cooled and a small aliquot of reaction mixture was taken for ^{1}H NMR spectroscopy to determine the conversion. When no further conversion was noted, the polymerization mixture was transferred into a round-bottom flask with CH_2Cl_2 (3−5 mL), and the polymer was precipitated from addition of methanol (18−30 mL). After separation, the polymer was dried *in vacuo* to constant weight to determine the yield. Molecular weight (M_n) and PDIs were determined by GPC using polystyrene standards.

Hydrolysis of Polymers and Chiral GC Analysis. In a typical procedure, a small round-bottom flask was loaded with polycarbonate (20 mg, 0.141 mmol) and NaOH (11 mg, 0.281 mmol) in MeOH (4 mL). The mixture was refluxed for 3 h and then neutralized with HCl(aq) (1 M). The crude mixture was then extracted with ether. After drying over anhydrous $MgSO_4$, a small aliquot was injected into a GC equipped with a Cyclodex-B column to determine the enantiomeric excess of the 1,2-*trans*-cyclohexanediol (t_R = 14.32 min for (*S,S*)-1,2-*trans*-cyclohexanediol, t_R = 14.75 min for (*R,R*)-1,2-*trans*-cyclohexanediol).

X-ray Crystallography. All data for compounds **2a**, **2d**, and **2k** were collected on a Bruker APEX-II CCD diffractometer. The intensity data were corrected for absorption and decay (SADABS).[42] The data were integrated with SAINT,[43] and the structure was solved and refined using SHELXTL.[44] The factors for the determination of the absolute structure were refined according to established

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procedures.[45] Residue electrons were noted in the lattice of **2k**, which were found with the SQUEEZE routine from the PLATON package[46] to be the toluene solvate. X-ray crystal data, data collection parameters, and refinement parameters are summarized in Table 1, and further crystallographic details can be found in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Figures of representative ^{1}H NMR spectra of zinc complexes, GPC of polycarbonates, and a table showing observed and calculated tetrad distributions of PCHC in pdf format and X-ray crystal data files for **2a**, **2d**, and **2k** in cif format. 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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