

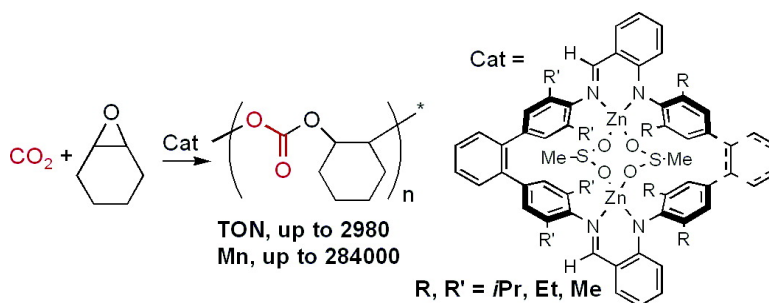
Article

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## Bimetallic Anilido-Aldimine Zinc Complexes for Epoxide/CO<sub>2</sub> Copolymerization

Bun Yeoul Lee,<sup>\*,†</sup> Heon Yong Kwon,<sup>†</sup> Su Yeon Lee,<sup>†</sup> Sung Jae Na,<sup>†</sup> Song-i Han,<sup>†</sup>  
Hoseop Yun,<sup>†</sup> Hyosun Lee,<sup>‡</sup> and Young-Whan Park<sup>‡</sup>

Contribution from the Department of Molecular Science and Technology, Ajou University, Suwon 443-749 Korea, and LG Chem Ltd./Research Park, 104-1, Munji-dong, Yuseong-gu, Daejeon 305-380, Korea

Received October 26, 2004; E-mail: bunyeoul@ajou.ac.kr

**Abstract:** Acyclic *o*-phenylene-bridged bis(anilido-aldimine) compounds,  $\sigma\text{-C}_6\text{H}_4\{\text{C}_6\text{H}_2\text{R}_2\text{N}=\text{CH}-\text{C}_6\text{H}_4-(\text{H})\text{N}(\text{C}_6\text{H}_3\text{R}'_2)\}_2$  and related 30-membered macrocyclic compounds,  $\sigma\text{-C}_6\text{H}_4\{\text{C}_6\text{H}_2\text{R}'_2\text{N}=\text{CH}-\text{C}_6\text{H}_4-(\text{H})\text{N}-\text{C}_6\text{H}_2\text{R}_2\}_2$  ( $\sigma\text{-C}_6\text{H}_4$ ) are prepared. Successive additions of  $\text{Me}_2\text{Zn}$  and  $\text{SO}_2$  gas to the bis(anilido-aldimine) compounds afford quantitatively dinuclear  $\mu$ -methylsulfinato zinc complexes,  $\sigma\text{-C}_6\text{H}_4\{\text{C}_6\text{H}_2\text{R}_2\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{N}(\text{C}_6\text{H}_3\text{R}'_2)-\kappa^2\text{-N,N}\}\text{Zn}(\mu\text{-OS}(\text{O})\text{Me})_2$  (R = *i*Pr and R' = *i*Pr, **29**; R = Et and R' = Et, **30**; R = Me and R' = Me, **31**; R = Me and R' = *i*Pr, **32**; R = Et and R' = Me, **33**; R = Et and R' = *i*Pr, **34**; R = *i*Pr and R' = Et, **35**) and  $\sigma\text{-C}_6\text{H}_4\{\text{C}_6\text{H}_2\text{R}'_2\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{N}-\text{C}_6\text{H}_2\text{R}_2-\kappa^2\text{-N,N}\}\text{Zn}(\mu\text{-OS}(\text{O})\text{Me})_2$  ( $\sigma\text{-C}_6\text{H}_4$ ) (R = Et and R' = Et, **36**; R = Me and R' = Me, **37**; R = *i*Pr and R' = Me, **38**; R = Et and R' = Me, **39**; R = Me and R' = *i*Pr, **40**). Molecular structures of **34** and **40** are confirmed by X-ray crystallography. Complexes **30–35** show high activity for cyclohexene oxide/CO<sub>2</sub> copolymerization at low [Zn]/[monomer] ratio (1:5600), whereas the complex of mononucleating  $\beta$ -diketiminato  $\{[(\text{C}_6\text{H}_3\text{Et}_2)\text{N}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{Et}_2)]\text{Zn}(\mu\text{-OS}(\text{O})\text{Et})_2\}$  shows negligible activity in the same condition. Activity is sensitive to the *N*-aryl ortho substituents and the highest activity is observed with **32**. Turnover number up to 2980 and molecular weight ( $M_n$ ) up to 284 000 are attained with **32** at such a highly diluted condition as [Zn]/[monomer] = 1:17 400. Macrocyclic complexes **36–40** show negligible activity for copolymerization.

### Introduction

Bimetallic catalysis has been commonly observed in metalloenzymes, and scientific activities have been devoted not only to reveal its action but also to mimic its advantageous characteristics by constructing bimetallic systems.<sup>1</sup> Asymmetric aldol condensation by bimetallic zinc complexes<sup>2</sup> and polym-

erization reaction by dinuclear homogeneous Ziegler–Natta catalysts<sup>3</sup> are among the typical examples. To achieve the cooperative action of the two metal centers that is exhibited by natural metalloenzymes, the two metals should be suitably arranged in space by the construction of a well-designed ligand system. Recently, a large number of  $\beta$ -diketiminato complexes have been reported in bioorganic, main-group, and transition-metal chemistry.<sup>4</sup> We envisaged synthesis of bis(diketimine) compounds such as **I** and **II**. A macrocyclic compound of type **II** with R = H was recently reported but the metal complexes derived from the compound either are not soluble or decompose in common organic solvents, thus hampering further studies.<sup>5</sup> Most of the recently reported  $\beta$ -diketiminato complexes are those derived from ligands bearing *N*-aryl ortho substituents. The substituents endow the complexes not only with enhanced solubility but also with more stability. Furthermore, the structure and the reactivity are highly sensitive to the *N*-aryl ortho substituents. Synthesis and application of macrocyclic compounds is also currently a hot research field in supramolecular chemistry.<sup>6</sup> In the dinuclear complexes derived from **I** and **II**, the two metals are situated opposite each other at a distance of

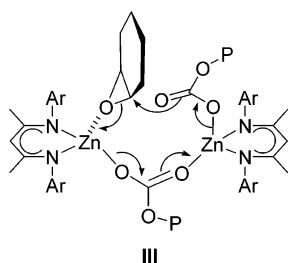
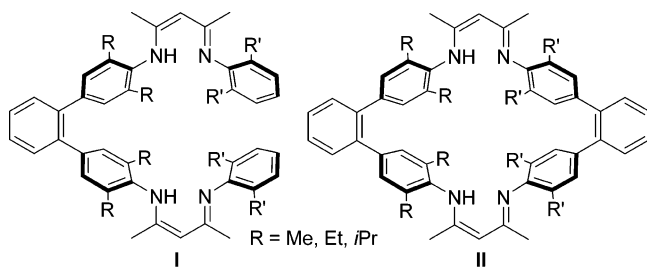
<sup>†</sup> Ajou University.

<sup>‡</sup> LG Chem Ltd.

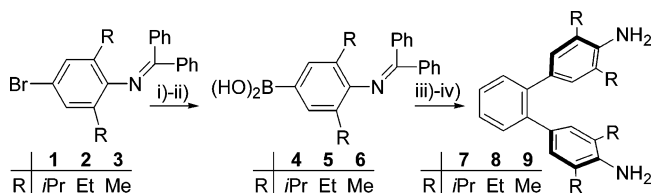
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~5 Å, and consequently cooperative actions of the two metal centers are to be expected in some catalysis reactions.



Coates et al.<sup>7-9</sup> have shown that the  $\beta$ -diketiminato zinc complexes can serve as catalysts for epoxide/ $\text{CO}_2$  copolymerization. The activity is highly sensitive to the *N*-aryl ortho substituents. They attributed this sensitivity to the formation of an associated bimetallic active species and proposed bimetallic catalytic action as **III**.<sup>8</sup> If the substituents are too small, such as methyl, the complex forms a tightly bound bimetallic complex, which is not active. If the substituents are too large, the complex cannot form the bimetallic species and this results

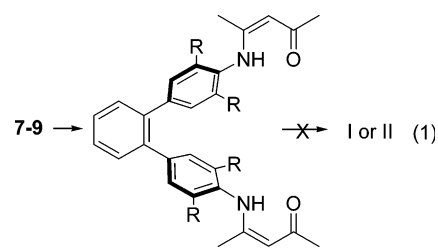
Scheme 1<sup>a</sup>

<sup>a</sup> (i) *n*-BuLi; (ii) B(OiPr)<sub>3</sub>; (iii) 1,2-dibromobenzene, Pd(PPh<sub>3</sub>)<sub>4</sub> (3 mol %), Na<sub>2</sub>CO<sub>3</sub>; (iv) HCl.

in reduced activity. Even though the  $\beta$ -diketiminato zinc complexes have a strong tendency to form the associated dinuclear species in solution, the probability for the complexes to be present as the relatively less active monomeric species is increased by reducing the concentration of the catalyst, that is, by reducing the [Zn]/[monomer] ratio in neat polymerization conditions. Dissociation to less active monomeric species can be excluded for bimetallic zinc complexes derived from **I** and **II**, and hence high activity is expected even at a low [Zn]/[monomer] ratio. By realization of high activity at the low mole ratio, increase of turnover number (TON) and concomitant increase of molecular weight by its living polymerization character are expected. The copolymer shows brittle character.<sup>10</sup> Increasing the molecular weight may be one of the tools to overcome the brittleness.

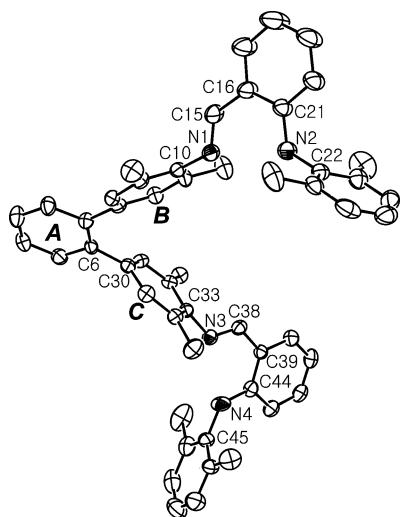
## Results and Discussion

**Synthesis and Characterization.** Key building blocks for constructing compounds **I** and **II** are the 4,4'-diamino-*o*-terphenyl derivatives bearing alkyl substituents at the 3, 5, 3'', and 5'' positions, for which the synthetic route is shown in Scheme 1. *N*-Diphenylmethylene-2,6-dialkyl-4-bromoanilines **1-3** are prepared in 50-g scale by the tetraethyl orthosilicate-mediated Schiff base condensation of benzophenone with the corresponding 2,6-dialkyl-4-bromoanilines.<sup>11</sup> The diphenylketimine functional group is stable to lithiation conditions [*n*-BuLi, tetrahydrofuran (THF), -78 °C]<sup>12</sup> and hence the bromo compounds **1-3** can be converted to boronic acids **4-6** by the conventional method, in good yields (82–87%). Suzuki coupling reactions of the boronic acids with 1,2-dibromobenzene and subsequent hydrolysis of the diphenylketimine group under acidic conditions affords blue fluorescent diamino compounds **7-9** in 82–87% yields. The synthetic method is so straightforward that **7** can be synthesized in 7-g scale without any chromatographic purification procedure. Since various Schiff base metal complexes of bulky 2,6-diisopropylaniline have been developed as precursors for olefin polymerization catalysts,<sup>13</sup> compounds **7-9** may be used as building blocks to construct such bimetallic complexes.



Reaction of **7-9** with excess 2,4-pentanedione affords the desired  $\beta$ -ketoamines, but various attempts to construct com-

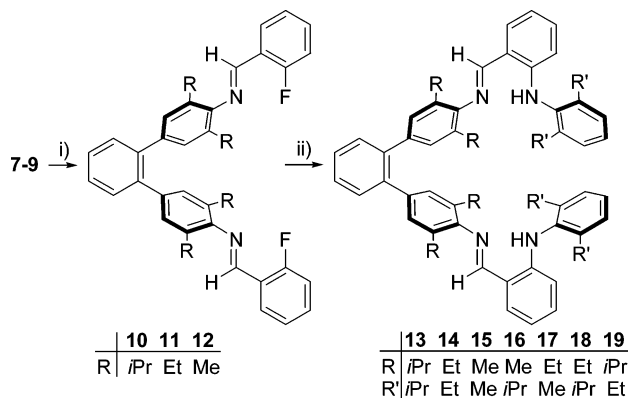
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**Figure 1.** Thermal ellipsoid plot (30% probability level) of **15**. Selected bond distances (in angstroms) and angles (in degrees): N(1)–C(15), 1.266(5); C(15)–C(16), 1.456(6); C(16)–C(21), 1.404(6); N(2)–C(21), 1.379(6); N(3)–C(38), 1.275(5); C(38)–C(39), 1.459(6); C(39)–C(44), 1.421(6); N(4)–C(44), 1.354(6); C(15)–N(1)–C(10), 117.6(4); N(1)–C(15)–C(16), 126.1(5); C(21)–N(2)–C(22), 123.8(5); C(38)–N(3)–C(33), 121.8(4); N(3)–C(38)–C(39), 124.8(5); C(44)–N(4)–C(45), 126.8(5).

pounds of types **I** or **II** from the  $\beta$ -ketoamines were not successful (eq 1). Instead of constructing **I** and **II**, syntheses of related anilido-aldimine compounds were pursued (Scheme 2).<sup>14</sup>

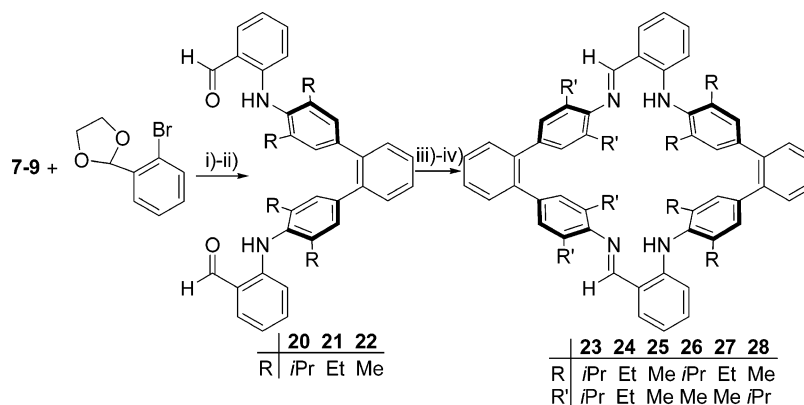
#### Scheme 2<sup>a</sup>



<sup>a</sup> (i) 2-Fluorobenzaldehyde; (ii) Li(H)N–C<sub>6</sub>H<sub>3</sub>R'<sub>2</sub>.

Schiff bases **10–12** are prepared by the conventional method in good yields (73–87%). Nucleophilic aromatic substitution

#### Scheme 3<sup>a</sup>



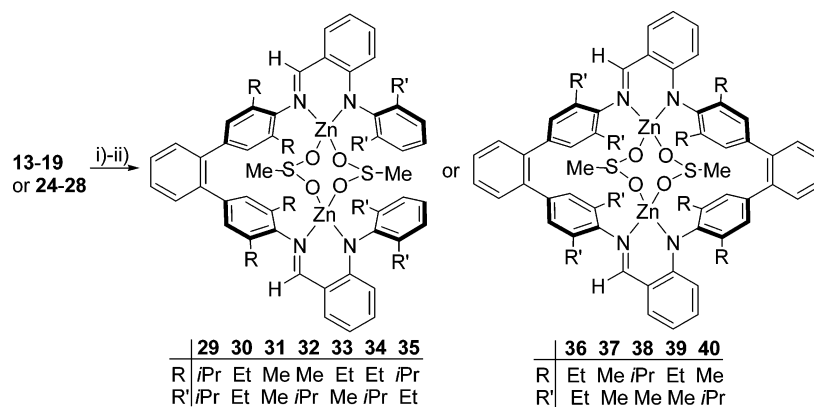
<sup>a</sup> (i) Pd(OAc)<sub>2</sub> (0.8 mol %), DPEphos (1.2 mol %), NarOBu; (ii) HCl; (iii) HCl salt of **7–9**; (iv) aq NaHCO<sub>3</sub>.

of the fluoride with Li(H)NAr affords the desired bis(anilido-aldimine) compounds **13–19** in excellent yields (86–95%). The <sup>1</sup>H and <sup>13</sup>C NMR spectra and the elemental analysis data are in agreement with the structures, and the connectivity of **15** is confirmed by X-ray crystallography (Figure 1).

Thirty-membered macrocyclic bis(anilido-aldimine) compounds are also effectively synthesized as well. The synthetic route used for constructing the acyclic bis(anilido-aldimine) compounds **13–19** (Scheme 2) does not work in these cases and another was devised (Scheme 3). An amination reaction of **7–9** with 1,3-dioxolane-protected 2-bromobenzaldehyde and subsequent deprotection of the dioxolane group furnishes **20–22** in 73–87% yields.<sup>15</sup> Cyclization is carried out by refluxing the aldehydes with HCl salts of **7–9** in ethanol for several days. HCl salts of the cyclized compounds are deposited from the ethanol solution and neutralized with aqueous NaHCO<sub>3</sub> solution. The macrocyclic compounds **23–28** are routinely purified by column chromatography on silica gel and the isolated yields are exceptionally high (73–88%). The high yields may be attributed to a proton-template effect or to rigidity of the macrocycles.<sup>16</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra and fast atom bombardment (FAB) mass data are in agreement with the ring structure.

Reactions of **13–19** and **24–28** with excess Me<sub>2</sub>Zn furnish quantitatively the desired dinuclear methylzinc complexes (Scheme 4). In the <sup>1</sup>H NMR spectra, the N–H proton signals that are observed in the 10–11 ppm range for **13–19** and **23–28** completely disappear and new Zn–CH<sub>3</sub> proton signals appears at –0.5 to –1.0 ppm as singlets. The <sup>1</sup>H NMR study indicates that the corresponding reaction of the macrocyclic compound **23**, which bears isopropyl groups on both sides, gives cleanly a monometalated complex. Even heating to 80 °C for several days does not provide the desired dinuclear complex. Because  $\beta$ -diketiminato alkoxy or acetoxy zinc complexes are reported to be effective catalysts for epoxide/CO<sub>2</sub> copolymerization, transformation of the methylzinc complexes to the corresponding alkoxy or acetoxy complexes by treatment of methanol or acetic acid were attempted, but the trails were unsuccessful. The demetalated ligands were the main products.

Because alkylsulfinato complexes likewise were reported to be active initiators for the epoxide/CO<sub>2</sub> copolymerization, transformation of the methylzinc complexes to the corresponding methylsulfinato complexes was pursued (Scheme 4).<sup>17</sup> Addition of anhydrous SO<sub>2</sub> gas to the methylzinc complexes results in

Scheme 4<sup>a</sup>

<sup>a</sup> (i) Me<sub>2</sub>Zn; (ii) SO<sub>2</sub>.

several sets of rather complex <sup>1</sup>H and <sup>13</sup>C NMR signals. The Zn–CH<sub>3</sub> signal is completely removed but several new singlet signals, which can be assigned to S–CH<sub>3</sub>, are observed in the 1–2 ppm range in the <sup>1</sup>H NMR spectra (C<sub>6</sub>D<sub>6</sub>, 25 °C). Three N=CH signals are observed at 8.10, 8.07, and 8.04 ppm in 0.43:0.31:0.26 ratio as singlets in the <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 25 °C) of **29**, and four S–CH<sub>3</sub> signals are observed as singlets at 1.93, 1.83, 1.65, and 1.53 ppm in 0.15:0.26:0.43:0.15 ratio. Three S–C signals are also observed at 48.01 (weak), 46.89 (strong), and 48.06 (weak) ppm in the <sup>13</sup>C NMR spectrum. These observations may be explained by isomerism that arises from the tetrahedral nature of the sulfur atom and the dinuclear  $\mu$ -methylsulfinate structure shown in Scheme 4. The similar  $\mu$ -ethylsulfinate-bridged structure was also observed for mono-nucleating  $\beta$ -diketiminato complexes.<sup>17</sup> For the  $\mu$ -methylsulfinate structure, three isomers are possible from the relative configurations of the methyls at the tetrahedral sulfur centers, as shown in Figure 2. For isomer A, the two S–CH<sub>3</sub> methyls

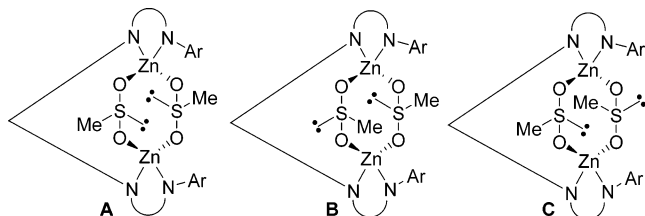


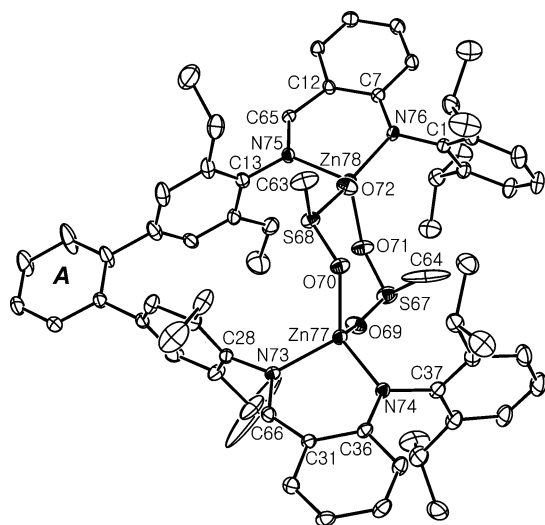
Figure 2. Possible isomers for **29**–**35**.

are not equivalent and observation of two separate signals is expected in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. For the B and C isomers, the two methyls are equivalent and hence a single signal is expected. Observation of three N=CH signals in 0.43:0.31:0.26 ratio and four S–CH<sub>3</sub> signals in 0.15:0.26:0.43:0.15 ratio can be well interpreted as the presence of the three isomers. Observation of three S–CH<sub>3</sub> signals instead of four in the <sup>13</sup>C NMR is probably due to collapse of two signals to a single one. The same three sets of signals are observed in the <sup>1</sup>H NMR spectra of **30** and **35**. In these cases, four S–CH<sub>3</sub> carbon signals

are fully observed in the <sup>13</sup>C NMR spectra. Only a set of signals is observed for **31** and a set of signals is dominant with minimal amounts of minor isomers (less than 10%) for **32**–**34**. When the temperature is increased to 100 °C in the <sup>1</sup>H NMR study (toluene-*d*<sub>8</sub>), several sets of signals collapse to a set of signals for all complexes. The signals for the bis(anilido-imine) ligand frame are sharp although the S–CH<sub>3</sub> signals are very broad at 1.5–2.0 ppm. Similarly, several sets of signals (two sets for **36**–**37** and **39**–**40** and three sets for **38**) are observed for the macrocyclic complexes in the room-temperature <sup>1</sup>H NMR spectra, but in these cases too, the sets of signals collapse to a set on heating to 100 °C in toluene-*d*<sub>8</sub>. Contrasting with the observation of broad S–CH<sub>3</sub> signals for **29**–**35**, sharp S–CH<sub>3</sub> signals are observed in the high-temperature <sup>1</sup>H NMR spectra of the macrocyclic complexes **36**–**40**. Single crystals suitable

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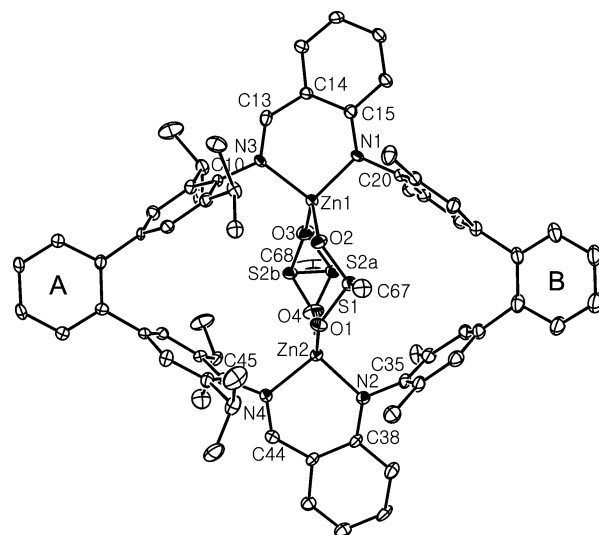


**Figure 3.** Thermal ellipsoid plot (30% probability level) of **34**. Selected bond distances (in angstroms) and angles (in degrees): N(75)–Zn(78), 1.984(4); N(73)–Zn(77), 2.000(4); N(76)–Zn(78), 1.938(4); N(74)–Zn(77), 1.938(4); O(71)–Zn(78), 1.963(4); O(72)–Zn(78), 1.969(3); O(69)–Zn(77), 1.943(3); O(70)–Zn(77), 1.990(3); C(65)–N(75), 1.304(5); C(66)–N(73), 1.290(5); C(7)–N(76), 1.358(6); C(36)–N(74), 1.360(5); C(65)–N(75)–C(13), 116.2(4); C(66)–N(73)–C(28), 116.9(4); C(7)–N(76)–C(1), 120.1(4); C(36)–N(74)–C(37), 117.4(4); N(76)–Zn(78)–N(75), 97.35(15); N(74)–Zn(77)–N(73), 96.15(15); O(71)–Zn(78)–O(72), 103.61(15); O(69)–Zn(77)–O(70), 103.96(14); O(70)–S(68)–O(72), 109.2(2); O(70)–S(68)–C(63), 99.4(2); O(72)–S(68)–C(63), 99.0(3); Zn(77)–Zn(78), 4.867.

for X-ray crystallography are obtained for complexes **34** and **40**, where one isomer is predominant at room temperature, and their molecular structures have been confirmed by X-ray crystallography (Table 2, Figures 3 and 4).

**X-ray Crystallographic Studies.** Figure 1 shows an Ortep drawing of **15** with selected bond distances and angles. The metal binding sites are not situated opposite each other as in the macrocyclic compounds **23–28**. Interestingly, the C benzene ring is situated slightly bent away from the B ring, which is measured by deviation of the C6–C30–C33 angle from the normal 180° to 169.9°. The same directional bending of the N3 atom from its normal position is also observed (C30–C33–N3 angle, 169.6°). These deviations are probably due to the repulsion between the  $\pi$ -electrons on the B and C rings.

Figure 3 shows the  $\mu$ -methylsulfinate structure of **34**. It reveals an eight-membered jagged metallacycle with a Zn–Zn separation of 4.867 Å, a distance slightly shorter than that observed for the associated dimeric  $\beta$ -diketiminato complex  $\{[(C_6H_3iPr_2)N=C(Me)CH=C(Me)N(C_6H_3iPr_2)]Zn(\mu-EtSO_2)\}_2$  (4.98 Å).<sup>17</sup> Each zinc atom is situated on a plane formed by the chelated ligand (dihedral angles of C31–C66–N73–Zn77 and C12–C65–N75–Zn78,  $-2.2^\circ$  and  $0.1^\circ$ , respectively), which contrasts with the observation of a slightly puckered structure found in  $\{[(C_6H_3iPr_2)N=C(Me)CH=C(Me)N(C_6H_3iPr_2)]Zn(\mu-EtSO_2)\}_2$  (the corresponding dihedral angle,  $7.2^\circ$ ).<sup>17</sup> Almost perpendicular arrangements between the chelated six-membered rings and the benzene rings attached to them are observed. The C=N(imine) distances [1.304(5) and 1.290(5) Å] are increased by the coordination of zinc [the corresponding distances in **15**, 1.266(5) and 1.275(5) Å] while the C–N(anilido) distances are not altered severely by the coordination. The N(imine)–ring A(centroid)–N(imine) angle ( $57.41^\circ$ ) is substantially reduced by the coordination (the corresponding angle for **15**,  $78.95^\circ$ ), which triggers a reduction of the N(imine)–N(imine) separation (6.829



**Figure 4.** Thermal ellipsoid plot (30% probability level) of **40**. Selected bond distances (in angstroms) and angles (in degrees): Zn(1)–N(3), 1.978(5); Zn(2)–N(4), 1.978(5); Zn(1)–N(1), 1.928(5); Zn(2)–N(2), 1.939(5); Zn(1)–O(2), 1.943(4); Zn(1)–O(3), 1.946(4); Zn(2)–O(1), 1.947(4); Zn(2)–O(4), 1.955(4); C(13)–N(3), 1.307(8); C(44)–N(4), 1.294(7); C(15)–N(1), 1.350(7); C(38)–N(2), 1.352(7); C(13)–N(3)–C(10), 122.9(5); C(44)–N(4)–C(45), 121.8(5); C(15)–N(1)–C(20), 122.0(5); C(38)–N(2)–C(35), 123.0(5); N(1)–Zn(1)–N(3), 97.5(2); N(2)–Zn(2)–N(4), 98.1(2); O(2)–Zn(1)–O(3), 110.93(19); O(1)–Zn(2)–O(4), 109.74(19); Zn(1)–Zn(2), 4.690.

and 8.987 Å for **34** and **15**, respectively). The N(anilido)–N(anilido) separation (7.988 Å) is significantly longer than the N(imine)–N(imine) separation (6.829 Å).

Solid structure of **40** is shown in Figure 4 with selected bond distances and angles. One of the two CH<sub>3</sub>–S fragments is disordered. By forming a macrocyclic ligand framework, both the Zn–Zn separation (4.690 and 4.867 Å for **40** and **34**, respectively) and the N(anilido)–N(anilido) separation (7.365 and 7.988 Å for **40** and **34**, respectively) are contracted while the N(imine)–N(imine) separation (7.139 and 6.829 Å for **40** and **34**, respectively) is elongated. The reduced Zn–Zn separation induces not only reduction of the average Zn–O distance (1.948 and 1.966 Å for **40** and **34**, respectively) but also increase of the O–Zn–O angle (average  $110.34^\circ$  and  $103.79^\circ$  for **40** and **34**, respectively). Both the reduced Zn–O distance and the shift of the O–Zn–O angles close to the ideal tetrahedral value may imply that the methylsulfinate ligand is more tightly bound in the macrocyclic complex **40**. The N(imine)–ring A(centroid)–N(imine) and the N(anilido)–ring B(centroid)–N(anilido) angles are close to the ideal value of 60° ( $60.46^\circ$  and  $62.37^\circ$ , respectively). Each zinc atom is situated in a plane formed by the chelated ligand and the two chelated six-membered rings are situated almost in a plane [angle between the planes,  $2.91(23)^\circ$ ].

**Polymerization Studies.** The main expected advantage of the complexes **29–40** for epoxide/CO<sub>2</sub> copolymerization is that they can form a dinuclear active species, as proposed by Coates and co-workers,<sup>8</sup> even at a low [Zn]/[monomer] ratio. They usually carried out the copolymerization reactions with the  $\beta$ -diketiminato zinc complexes in a neat monomer with [Zn]/[monomer] = 1:1000.<sup>7,8</sup> In that situation, the attainable maximum TON is limited to 1000 and actually it is further limited to  $\sim 500$  by the limited conversion ( $\sim 50\%$ ) caused by viscosity. Because the catalyst shows living character, the molecular

**Table 1.** Cyclohexene Oxide (CHO)/CO<sub>2</sub> Copolymerization Results<sup>a</sup>

entry	catalyst	time (h)	TON <sup>b</sup>	TOF <sup>c</sup>	% carbonate <sup>d</sup>	<i>M<sub>n</sub></i> <sup>e</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>e</sup>
1	29			<i>f</i>			
2	30	10	1680	168	96	129 000	1.3
3	31	10	1060	106	93	80 000	1.3
4	32	5	1560	312	94	225 000	1.7
5 <sup>g</sup>	32	10	2720	272	91	261 000	1.6
6 <sup>h</sup>	32	15	2980	200	91	284 000	1.7
7	33	10	670	67	93	77 000	1.3
8	34	5	1450	290	93	205 000	1.6
9	35	10	670	67	85	88 000	1.3
10	36–40	10	<i>f</i>				
11	BDI <sup>i</sup>	10	56	5.6	74	27 000	1.8

<sup>a</sup> Polymerization conditions: neat CHO (8.0 mL, 79 mmol), [Zn]/[CHO] = 1:5600, 80 °C, 12 bar of CO<sub>2</sub> (initial pressure). <sup>b</sup> Turnover number in moles of CHO consumed per mole of Zn. <sup>c</sup> Turnover frequency in moles of CHO consumed per mole of Zn per hour. <sup>d</sup> Estimated by <sup>1</sup>H NMR spectroscopy. <sup>e</sup> Determined by GPC, calibrated with polystyrene standard in THF. <sup>f</sup> Negligible. <sup>g</sup> Neat CHO (16 mL), [Zn]/[CHO] = 1:11 200. <sup>h</sup> Neat CHO (24 mL), [Zn]/[CHO] = 1:16 800. <sup>i</sup> BDI = {[C<sub>6</sub>H<sub>3</sub>Et<sub>2</sub>]N=C(Me)CH=C(Me)N(C<sub>6</sub>H<sub>3</sub>Et<sub>2</sub>)Zn(μ-OS(O)Et)}<sub>2</sub>.

weight of the obtained polymer is governed by the TON. To achieve high TON, and consequently to obtain high molecular weight polymer, the [Zn]/[monomer] ratio should be reduced. The zinc complexes constructed from the mononucleating β-diketiminato ligands exist in an equilibrium involving monomeric and associated dimeric species. Even though some complexes strongly favor the active dimeric species, the probability for the less active monomeric species increases by reducing the mole ratio, which might result in low activity under low mole ratio conditions. Recently, [ArN=C(Me)CH=C(Me)-NAr]ZnN(SiMe<sub>3</sub>)<sub>2</sub> (Ar = 2,6-diethylphenyl or 2,6-diisopropylphenyl), which showed high activity at the relatively high [Zn]/[cyclohexene oxide] ratios of 1:1700 and 1:1000, was reported to show negligible activity (TOF 32) at the low mole ratio of [Zn]/[cyclohexene oxide] = 1:3300.<sup>18</sup>

The standard polymerization condition is set at a more dilute [Zn]/[cyclohexene oxide] = 1:5800 to ascertain if **29–40** show high activity even at the low mole ratio. Dissociation to the less active monomeric species can be excluded for **29–40**. To realize the polymerization activity at such a low concentration of catalysts, the cyclohexene oxide (CHO) and CO<sub>2</sub> should be rigorously purified (see Experimental Section in the Supporting Information). Under standard conditions, a negligible amount of polymer (TON 56, TOF 5.6; entry 11 in Table 1) is obtained with {[C<sub>6</sub>H<sub>3</sub>Et<sub>2</sub>]N=C(Me)CH=C(Me)N(C<sub>6</sub>H<sub>3</sub>Et<sub>2</sub>)Zn(μ-OS(O)Et)}<sub>2</sub>, which was reported to show high activity at high [Zn]/[CHO] ratio of 1:1000 (TON 328, TOF 164).<sup>17</sup> The complex is chosen as a comparison catalyst because the corresponding acetoxy derivative was reported to have the strongest tendency to form the associated dimeric species, even at high temperature.<sup>8</sup> As expected, all acyclic bis(anilido-imine) complexes except **29** show high activity under standard conditions. The turn of frequency (TOF) is still sensitive to the *N*-aryl ortho substituents, as is observed for the zinc complexes of the mononucleating β-diketiminates. In the standard polymerization, the solution is stirred by using a magnetic stirring bar, and in that case, maximum conversion was limited to ~30% by viscosity, which limited the attainable TON to ~1700. The complex **32**, bearing methyl and isopropyl groups, and complex

**34**, bearing ethyl and isopropyl groups, are so highly active that the limited TONs (1560 and 1450, respectively) are almost achieved in 5 h (entries 4 and 8). The TOFs are calculated to be 312 and 290, respectively, and these values are substantially higher when compared with that observed for {[C<sub>6</sub>H<sub>3</sub>Et<sub>2</sub>]N=C(Me)CH=C(Me)N(C<sub>6</sub>H<sub>3</sub>Et<sub>2</sub>)Zn(μ-OS(O)Et)}<sub>2</sub> at high [Zn]/[CHO] ratio of 1:1000 (TOF 164).<sup>17</sup> Coates and co-workers<sup>8</sup> reported that the zinc β-diketiminato complex, where both aryls are 2,6-dimethylphenyl, is totally inactive because of formation of tightly bound associated dimeric species, but the bis(anilido-imine) complex **31**, where both aryls bear methyl substituents, shows fairly good activity (entry 3). Noteworthy is that **35**, which bears the isopropyl group in its imine moiety and ethyl groups in the anilido moiety, shows low activity (TON 670, TOF 67) while **32**, which bears the same substituents but with their positions exchanged, is highly active (TON 1450, TOF 290). The TON of **32** can be almost doubled (TON 2720) by reducing the [Zn]/[CHO] ratio by 2-fold (1:11 200) and simultaneously increasing the reaction time by 2-fold (entries 4 and 5). When the mole ratio is reduced 3-fold (to 1:16 800) and the reaction time is tripled (to 15 h), the complex shows still a higher TON (2980) but it is not tripled (entry 6). Some deactivation by protic impurities in the monomer may be inevitable in that highly diluted condition, thus not giving the desired tripled TON.

The macrocyclic complexes **36–40** show negligible activity in the standard polymerization condition. This negligible activity is presumably attributed to the tight binding of the methylsulfinate ligand, which hampers the initiation reaction. Observation of the sharp S–CH<sub>3</sub> signals in the <sup>1</sup>H NMR spectra (100 °C, toluene-*d*<sub>8</sub>) of **36–40** and observation of the relatively short Zn–O distances and the ideal tetrahedral O–Zn–O angles in the X-ray structure of **40** support that the methylsulfinate is strongly bound in the preorganized macrocyclic rings, thus not permitting initiation.

As expected, molecular weights of the polymer can be increased by the increase of TONs and number-average molecular weight (*M<sub>n</sub>*) up to 284 000 is attained (entry 6). The reported molecular weights (*M<sub>n</sub>*) of the polymers obtained by the conventional zinc complexes of the mononucleating β-diketiminato ligands have not exceeded 50 000. Observation of rather broad molecular weight distributions (*M<sub>w</sub>*/*M<sub>n</sub>* 1.3–1.7) may be explained by some kind of chain transfer reaction at the high polymerization temperature (85–75 °C). Coates and co-workers<sup>7,8</sup> observed narrow molecular weight distributions at relatively lower polymerization temperature (50 °C), and Rieger and co-workers<sup>17</sup> also observed broadening of the molecular weight distribution by increasing the polymerization temperature to 70 °C. Molecular weights of polymers obtained in 5 h polymerization time are in good agreement with those calculated from the TONs (entries 4 and 8) but those of the polymers obtained in 10 or 15 h are rather lower than the calculated values, which implies that some kind of chain transfer reaction occurs during the long polymerization times. The main drawback of the CO<sub>2</sub>/CHO copolymer compared with the conventional bisphenol A-based polycarbonate is the brittleness.<sup>10</sup> The chain entanglement molar mass, *M<sub>e</sub>*, was reported to be about 15 000, which is comparable to that of brittle polystyrene but substantially higher than that of bisphenol A-based polycarbonate (1800). The increased molecular weight may induce to more

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**Table 2.** Crystallographic Parameters of **15**, **34**, and **40**

	15	34	40
formula	C <sub>52</sub> H <sub>50</sub> N <sub>4</sub>	C <sub>66</sub> H <sub>78</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> Zn <sub>2</sub> ·(C <sub>2</sub> H <sub>5</sub> O <sub>0.5</sub> )	C <sub>68</sub> H <sub>72</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> Zn <sub>2</sub>
fw	730.96	1223.34	1204.26
<i>T</i> , K	293(2)	150(2)	150(2)
<i>a</i> , Å	8.1137(5)	24.4623(10)	41.0701(2)
<i>b</i> , Å	13.1016(7)	12.9181(3)	15.8235(5)
<i>c</i> , Å	39.0663(14)	24.3219(10)	22.6557(8)
α, deg	90	90	90
β, deg	92.2016(3)	118.4620(10)	101.666(2)
γ, deg	90	90	90
<i>V</i> , Å <sup>3</sup>	4149.8(4)	6756.9(4)	14 419.2(7)
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>N</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>C</i> 2/ <i>c</i>
<i>D</i> (calc), g·cm <sup>-3</sup>	1.170	1.203	1.109
<i>Z</i>	4	4	8
μ, mm <sup>-1</sup>	0.068	0.819	0.767
no. of data collected	12 040	65 938	52 341
no. of unique data	3548	15 472	15 374
no. of variables	521	810	812
<i>R</i> (%)	0.0528	0.0717	0.0864
<i>R</i> <sub>w</sub> (%)	0.1026	0.2156	0.2650
goodness of fit	1.006	1.057	1.019

<sup>a</sup> Data collected with Mo Kα radiation [ $\lambda(\text{K}\alpha) = 0.7107 \text{ \AA}$ ];  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$  with  $F_o > 2.0\sigma(I)$ ;  $R_w = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o)^2]^{1/2}]^{1/2}$  with  $F_o > 2.0\sigma(I)$ .

efficient chain entanglements, consequently resulting in increased toughness.

The carbonate linkage is more than 90% for all polymers obtained by the catalysts showing high activity (entries 2–8). Only the polymer obtained by **35**, which shows relatively lower activity, has rather low carbonate linkage (85%). The copolymer obtained by the comparison catalyst under standard conditions contains a substantial amount of ether linkage (carbonate linkage, 74%). The <sup>1</sup>H NMR spectra of the polymerization solutions indicate that only a few percent (3–4%) of cyclic carbonate compound is formed during the polymerization.

## Conclusion

Acyclic bis(anilido-aldimine) compounds (**13**–**19** in Scheme 2) and 30-membered cyclic bis(anilido-aldimine) compounds (**23**–**28** in Scheme 3) have been prepared. Yields in the macrocyclic forming reaction are exceptionally high (73–88%). Dinuclear  $\mu$ -methylsulfinato zinc complexes (**29**–**40** in Scheme 4) have been prepared from the bis(anilido-aldimine) compounds by successive addition of Me<sub>2</sub>Zn and SO<sub>2</sub> gas. Solid structures of **34** and **40** have been determined by X-ray crystallography. The acyclic complexes **30**–**35** show high activity for cyclohexene oxide/CO<sub>2</sub> copolymerization even at low [Zn]/[monomer] ratio, typically 1:5600, whereas the  $\beta$ -dikeminate complex  $\{[(\text{C}_6\text{H}_3\text{Et}_2)\text{N}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{Et}_2)]\text{Zn}(\mu\text{-OS}(\text{O})\text{Et})_2\}$  shows negligible activity at the same condition.

Activity is sensitive to the *N*-aryl ortho substituents and the highest activity is observed with **32**, bearing methyl and isopropyl substituents. The complex shows high activity at extremely dilute conditions such as [Zn]/[monomer] = 1:16 800 and TON up to 2980 is attained. High molecular-weight polymers (*M<sub>n</sub>* up to 284 000) are obtained by the increase of TONs. The macrocyclic complexes **36**–**40** show negligible activity. While this work strongly supports the bimetallic mechanism proposed by Coates and co-workers<sup>8</sup> for the copolymerization of CHO/CO<sub>2</sub>, others such as Darensbourg and co-workers with (Salen)Cr(III) and Chisholm and co-workers with (porphyrin)Al(III) have observed a reaction pathway that involves only one metal center.<sup>9</sup> Different metals with different ligand sets may well react via different pathways.

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**Supporting Information Available:** CIF files for **15**, **34**, and **40** and Experimental Section (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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