Inorg. Chem. **2001,** *40,* 5051−5054

Three-Coordinate Zinc Amide and Phenoxide Complexes Supported by a Bulky Schiff Base Ligand

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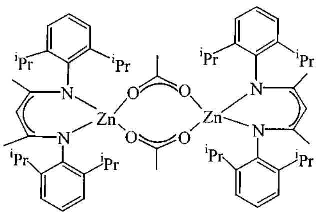
Received May 29, 2001

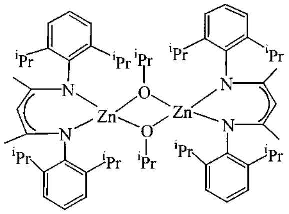
Introduction

There is considerable current interest in the ring-opening polymerization, ROP, of lactides and epoxides by discrete coordination complexes. The Darensbourg[1] group have had considerable success in ROP of cyclohexene oxide and the copolymerization of cyclohexene oxide, CHO, with CO_2 by the use of zinc phenoxide precursors of the form $Zn(OAr')_2L_2$, where OAr′ is a bulky phenoxide such as 2,6-$^tBu_2C_6H_3O$ and L is a labile ligand such as THF, Et_2O, or a tertiary phosphine. In their early work, it was not clear that mononuclear zinc species were catalytically active, and from more recent work from that laboratory where Ar′ is 2,6-$X_2C_6H_3-$ and X = F, Cl, and Br, it appears that dimeric species are the active species. Bridged complexes of the type $[L(Ar'O)Zn(\mu\text{-}OAr')]_2$ were structurally characterized, and the polymerization process was found to be dependent on the nature of OAr′, a fact which implicated their continued presence at the active site. While one OAr′ is used to initiate polymerization and becomes an end group, the other is involved in bridging to a neighboring zinc atom.

The Coates[2] group has employed the BDI ligand (2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene) as a spectator group bonded to zinc, and the dimeric acetate and isopropoxide shown in **A** and **B** have been used in the copolymerization of CHO and CO_2 and in lactide polymerization, respectively. A particularly interesting finding of the Coates group was that the isopropoxide species shown in **B** was capable of polymerizing *rac*-lactide to give mostly heterotactic polylactide, PLA. Given that the compound shown in **B** is not chiral, this result was attributed to chain end-group control wherein a lactide molecule with *R*,*R*-stereocenters preferentially inserts into a Zn-(*S*,*S*) chain and vice versa. In the CHO−CO_2 copolymerization, it was shown by polymer degradation that ring-opening of CHO occurred with inversion of configuration, i.e., by backside attack.

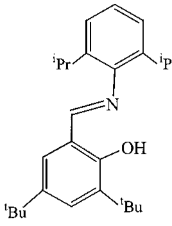


A

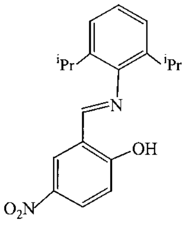


B

In this paper, we describe our preparation and characterization of some new zinc Schiff-base complexes of the form LZnX, where X = an aryloxide or amide, and L_2Zn, where L is one of the Schiff-base ligands shown in **C** and **D**. The reader may note that the ligand **C** is related to the BDI ligand employed by Coates et al. in their studies of **A** and **B**.



C



D

Experimental Section

General. All reactions, unless otherwise mentioned, were carried out under an atmosphere of N_2 purified over 4 Å molecular sieves. Flamed-out glassware and standard vacuum line, Schlenk, and N_2-atmosphere drybox techniques were employed. Benzene, toluene, ether, hexanes, and THF were distilled from purple solutions of sodium/benzophenone. Propylene oxide was distilled over calcium hydride, and carbon dioxide was purchased from BOC Gases. Bis(trimethylsilylamide) sodium salt and $ZnCl_2$ were purchased from Aldrich and used as received. Bis(trimethylsilylamide) zinc was prepared by reported procedures.[1] Lactide was sublimed twice prior to use. Elemental analyses were performed by Atlantic Microlab Inc. Free Schiff-base ligands were prepared by acid-catalyzed condensation following a literature procedure.[6]

$(L_C)ZnN(SiMe_3)_2$ (I). To a solution of 0.38 g (1.0 mmol) of $Zn(NSi_2Me_6)_2$ in 20 mL of toluene at −78 °C was slowly added 0.39 g (1.0 mmol) of free ligand **A** in 20 mL of toluene. The reaction mixture was allowed to warm to 22 °C and stirred for 3 h. Volatile components were evaporated under a dynamic vacuum, and the resulting yellow solid was washed with 3 × 5 mL of cold hexanes. Yield: 0.50 g, 81%. Subsequent to the initial submission of this work, the Darensbourg[1c] group also reported the preparation of this complex.

$(L_D)_2Zn$ (II). To a solution of 0.39 g (1.0 mmol) of $Zn(NSi_2Me_6)_2$ in 10 mL of toluene at −78 °C was slowly added 0.33 g (1.0 mmol) of free ligand **D** in 15 mL of toluene solution. The reaction mixture was allowed to warm to 22 °C and stirred for 3 h. Volatile components were evaporated under vacuum, and a yellow solid was obtained. Yield: 0.34 g, 94%. ^1H NMR (benzene-d_6, 400 MHz): δ 0.65 (bs, 12H, $CH(CH_3)_2$), 0.92 (d, J = 6.0 Hz, 12H, $CH(CH_3)_2$), 2.86 (m, 4H,

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10.1021/ic010560e CCC: $20.00

C*H*(CH$_3$)$_2$), 6.58 (s, 1H), 6.60 (s, 1H, C*H*), 6.86 (s, 2H, C*H*), 6.88 (s, 2H, C*H*), 6.98 (m, 2H, C*H*), 7.24 (s, 2H, C*H*), 7.70 (d, $J = 2.8$ Hz, 2H, C*H*), 7.86 (d, $J = 3.2$ Hz, 2H, C*H*), 7.89 (d, $J = 3.2$ Hz, 2H, C*H*). ^{13}C{H} (benzene-d_6, 100 MHz): δ 23.0, 24.6, 28.3, 116.1, 123.8, 124.5, 127.9, 128.5, 131.1, 134.1, 141.2, 145.4, 174.8, 176.4. Anal. Calcd for $C_{38}H_{42}N_4O_6Zn$: C, 63.73; H, 5.91; N, 7.82. Found: C, 63.95; H, 6.09; N, 7.63.

(L$_C$)Zn(2,6-di-^{t}butylphenoxide) (III). To a mixture of **I**, 0.41 g (0.66 mmol), and 2,6-di-^{t}butylphenol, 0.14 g (0.66 mmol), was added 30 mL of benzene. The mixture was stirred overnight at ambient temperature. Volatile components were evaporated under vacuum, and the resulting yellow solid was washed with 3 × 5 mL of cold hexanes. Yield: 0.37 g, 84%. ^{1}H NMR (benzene-d_6, 400 MHz): δ 0.91 (d, $J = 6.9$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, $J = 6.9$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (s, 9H, C(C*H*$_3$)$_3$), 1.46 (s, 9H, C(C*H*$_3$)$_3$), 1.64 (s, 18H, C(C*H*$_3$)$_3$), 2.99 (m, 2H, C*H*(CH$_3$)$_2$), 6.77(s, 1H), 6.90 (m, 1H) 7.02−7.15 (m, 3H), 7.34 (s, 1H), 7.36 (s, 1H), 7.69 (s, 1H), 7.88 (s, 1H). ^{13}C{H} (benzene-d_6, 100 MHz): δ 23.5, 25.0, 28.9, 29.6, 31.3, 31.6, 34.1, 35.4, 35.7, 116.9, 117.4, 124.4, 125.2, 128.5, 130.2, 132.7, 138.3, 139.5, 141.5, 143.1, 145.1, 164.6, 170.2, 176.5. Anal. Calcd for $C_{41}H_{59}NO_2Zn$: C, 74.24; H, 8.96; N, 2.11. Found: C, 73.84; H, 8.96; N, 2.08.

(L$_C$)$_2$Zn (IV). **I** (0.33 g, 0.53 mmol) in a Schlenk flask was heated overnight at 150 °C under vacuum, and Zn(NSi$_2$Me$_6$)$_2$ was distilled out and trapped. A bright yellow solid was obtained. Yield: 0.21 g, 93%. ^{1}H NMR (benzene-d_6, 250 MHz): δ 0.28 (d, 6H, $J = 6.8$ Hz, CH(C*H*$_3$)$_2$), 0.90 (d, 6H, $J = 6.8$ Hz, CH(C*H*$_3$)$_2$), 1.20 (s, 18H, CH(C*H*$_3$)$_2$), 1.22 (d, $J = 6.8$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, $J = 6.8$ Hz, 6H, CH(C*H*$_3$)$_3$), 1.62 (s, 18H, C(C*H*$_3$)$_3$), 2.65 (m, 2H, C*H*(CH$_3$)$_2$), 3.94 (m, 2H, C*H*(CH$_3$)$_2$), 6.74−7.86 (m, 12H, C*H*). ^{13}C{H} (benzene-d_6, 62.9 MHz): δ 22.7, 23.7, 25.0, 25.1, 28.1, 28.5, 30.1, 31.4, 33.9, 35.8, 117.2, 124.4, 124.6, 127.0, 130.3, 131.6, 135.7, 142.0, 142.1, 142.2, 147.6, 171.4, 176.2. Anal. Calcd for $C_{54}H_{76}N_2O_2Zn$: C, 76.25; H, 9.01; N, 3.29. Found: C, 75.34; H, 9.01; N, 3.27.

Polymerization of L-Lactide with I. To a mixture of 12 mg of **I** and 60 mg of L-lactide (ca. 20 equiv) in a NMR tube was added 0.5 mL of benzene-d_6. The reaction was then monitored by ^{1}H NMR spectroscopy. Over 80% of the monomer was converted to PLA in 3 h. ^{1}H and ^{13}C NMR data were consistent with the formation of isotactic PLA.[7]

Polymerization of *rac*-Lactide with I. To a mixture of 12 mg of **I** and 60 mg of *rac*-lactide (ca. 20 equiv) in a NMR tube was added 0.5 mL of benzene-d_6. The polymerization reaction was significantly slower than that with L-lactide. The solvent was then removed under vacuum, and the polymer was redissolved in CDCl$_3$. The proton-decoupled ^{1}H NMR and the ^{13}C{^{1}H} NMR spectra of the polymer showed that there was no stereoselectivity for the polymerizarion of *rac*-lactide with compound **I**.

Reaction of I with Propylene Oxide. PO (4.0 mL) was added to a Schlenk flask equipped with 47 mg of **I** and a stir bar. The mixture was then stirred for 3 days at ambient temperature. No PPO was obtained.

Reaction of I with CO$_2$. Carbon dioxide was introduced into a solution of 0.11 g (0.18 mmol) of **I** in 10 mL of benzene. The reaction mixture was stirred overnight at ambient temperature, during which a yellow precipitate formed. Volatile components were removed under vacuum and a yellow solid was obtained. Its IR spectrum did not show a characteristic C═O stretching frequency. This material had low solubility in common solvents such as benzene, THF, and methanol. Attempts to obtain crystals suitable for X-ray crystal analysis were not successful.

Copolymerization of Propylene Oxide and CO$_2$ with I. A stainless steel reactor was charged with a stir bar and 0.15 g (0.24 mmol) of **I**. After 8.5 mL (121.5 mmol**)** of PO was added, carbon dioxide was then introduced. The mixture was stirred overnight at 22 °C under a CO$_2$ pressure of 500 psi. No copolymer was obtained after workup of the reaction mixture.

X-ray Crystallography.[14] For crystals **I** and **II**, the data were collected using 5 s frames with an ω scan of 0.30°. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged using the Bruker SAINT software as well as utility programs from the XTEL library. An absorption correction was performed using the SADABS program supplied by Bruker AXS. The structures were solved using SHELXTL and Fourier techniques. All hydrogen atoms were clearly visible and were included as isotropic contributors in the final cycles of refinement. The data collection of **III** was done on a Nonius Kappa CCD diffractometer using 100 s frames with ω scans of 1.0°. Data integration was done with Denzo,[9] and scaling and merging of the data were done with Scalepack.[10] The structure was solved by the Patterson method in SHELXS-86.[11] Full-matrix least-squares refinements based on F^2 were performed in SHELXL-93.[12] The hydrogen atoms were included in the model at calculated positions using a riding model. Refinement of the Flack parameter[13] verified that this choice of enantiomer is correct. A summary of crystal data is given in Table 1.

Table 1. Selected Crystallographic Data for **I**−**III**

	I	**II**	**III**
empirical formula	$C_{33}H_{56}N_2OSi_2Zn$	$C_{38}H_{42}N_4O_6Zn$	$C_{41}H_{59}NO_2Zn$
fw	618.38	716.14	663.26
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a (Å)	10.7872(3)	14.501(4)	10.8679(1)
b (Å)	10.8787(3)	14.379(4)	18.0093(1)
c (Å)	17.4470(5)	20.191(4)	19.5705(1)
α (deg)	78.847(1)	90	
β (deg)	88.358(1)	107.00(1)	
γ (deg)	64.149(1)	90	
vol (Å^3)	1804.14	4031.20	3830.40
Z	2	4	4
calcd density (g/cm^3)	1.138	1.309	1.150
temp (K) of collection	113	115	200
indep reflns	8286	9259	8782
R	0.0280^a	0.0277^a	0.0405^b
R_w	0.0321^a	0.0254^a	0.0807^b
Flack param			−0.014(7)

[a] Refinement on F with $I > 2.33\sigma(I)$ and $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] Refinement on F^2 with all data and $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

Results and Discussion

Synthesis of Zinc Complexes. Preparation of the new compounds was carried out in toluene employing Zn(NSi$_2$Me$_6$)$_2$ and 1 equiv of the Schiff base. In the case of the protonated ligand shown in **C**, hereafter referred to as L$_C$H, the reaction proceeded to give (L$_C$)Zn(NSi$_2$Me$_6$) (**I**) and free HNSi$_2$Me$_6$. However, for the Schiff base shown in **D**, L$_D$H, the reaction did not stop at the monosubstituted product, but rather the bis-Schiff base complex (L$_D$)$_2$Zn (**II**) and the starting material amide were obtained. The differing reactivity is attributed to steric factors, and even compound **I** undergoes disproportionation upon heating to 150 °C under vacuum. Under these conditions,

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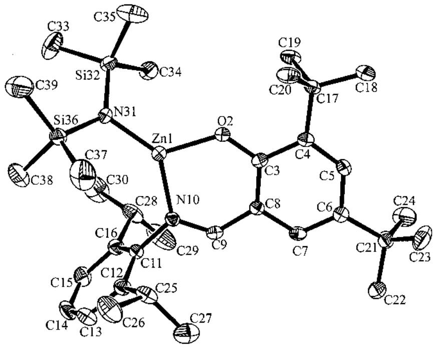

Figure 1. Molecular structure of compound **I**, $(L_C)ZnN(SiMe_3)_2$.

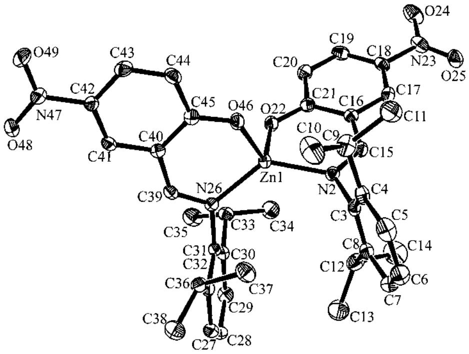

Figure 2. Molecular structure of compound **II**, $(L_D)_2Zn$.

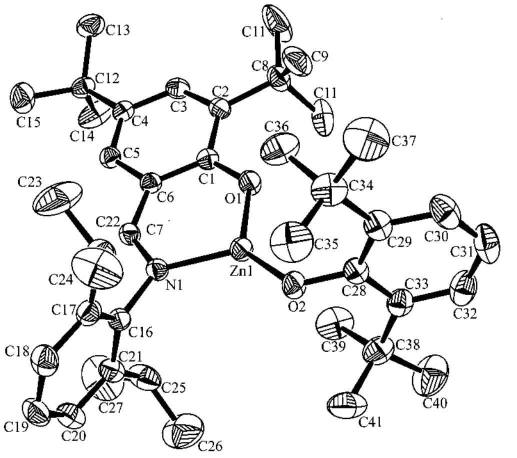

Figure 3. Molecular structure of compound **III** $(L_C)Zn$(2,6-di-^{t}butylphenoxide).

$Zn(NSi_2Me_6)_2$ distills, leading to $Zn(L_C)_2$ (**IV**). Compound **I** and the bulky phenol 2,6-${}^tBu_2C_6H_3OH$ react in benzene to give $(L_C)Zn(OC_6H_3$-2,6-${}^tBu_2)$ (**III**).

The new compounds are air-sensitive, crystalline materials and are soluble in aromatic hydrocarbon solvents. Compounds **I**, **II**, **III**, and **IV** are all yellow. It may be noted that the carbon content analysis of **IV** was low, although NMR spectra indicated that it was pure.

Solid-State and Molecular Structures. A summary of crystallographic data is given in Table 1, and ORTEP drawings of the molecular structures of compounds **I**, **II**, and **III** are given in Figures 1, 2, and 3, respectively. The compounds $(L_C)Zn(NSi_2Me_6)$ and $(L_C)Zn(OC_6H_3$-2,6-${}^tBu_2)$ provide relatively rare examples of three-coordinate monomeric planar zinc(II) complexes.[3] A summary of selected bond distances and angles is given in Table 2. In compound **I**, the Zn−N distance to the silylamide is notably shorter than to the Schiff base nitrogen. In **III**, the Zn−O distances to the 2,6-${}^tBu_2C_6H_3O$− and Schiff base ligands are less different though the Zn−O bond to the phenoxide is still shorter. The complexes are trigonal planar with the O−Zn−N angles of the Schiff base being less than 100°. In complex **I**, the O−Zn−N angle of 96° is very similar to that seen for the N−Zn−N angle of the BDI ligand in (BDI)-$Zn(NSi_2Me_6)$. In compound **II**, the four-coordinate and pseudotetrahedral zinc(II) ion has somewhat longer Zn−O and Zn−N distances as expected for a metal ion with a higher coordination number.

Table 2. Selected Bond Distances (Å)and Angles (deg) for Complexes **I**−**III**

	Complex **I**		
Zn1−O2	1.8859(19)	O2−Zn1−N10	95.99(9)
Zn1−N10	1.9805(23)	O2−Zn1−N31	127.26(9)
Zn1−N31	1.8689(24)	N10−Zn1−N31	136.69(10)
	Complex **II**		
Zn1−O22	1.9413(22)	O22−Zn1−O46	106.33(10)
Zn1−O46	1.9373(22)	O22−Zn1−N2	95.30(10)
Zn1−N2	1.9952(26)	O22−Zn1−N26	113.63(10)
Zn1−N26	1.9994(25)	O46−Zn1−N26	94.91(10)
		O46−Zn1−N2	115.43(10)
		N2−Zn1−N26	130.26(11)
	Complex **III**		
Zn1−O1	1.872(1)	O1−Zn1−N1	99.06(6)
Zn1−O2	1.818(1)	O2−Zn1−O1	128.75(6)
Zn1−N1	1.962(2)	O2−Zn1−N1	131.94(6)

Solution ${}^1H$ NMR Spectra. The ${}^1H$ NMR spectra for compounds **I** and **III** are particularly interesting in allowing for a comparison with related BDI complexes. The isopropyl methyl groups of the Schiff base ligands shown in **C** and **D** are equivalent as long as there is rapid rotation on the NMR time scale about the N−C(phenyl) bond. The ${}^1H$ NMR spectra of the free ligands, **C** and **D**, show just one isopropyl methyl doublet. However, when complexed to the zinc ion in compounds **I** and **III**, the ligand L_C displays two sets of isopropyl doublets but only one isopropyl methine septet, indicating that upon complexation the rotation about the N−C(phenyl) bond is slow or frozen out on the NMR time scale. This is similar to that seen for BDI isopropyl methyl groups in the complexes shown in **A** and **B**.[4] However, even the free ligand BDI shows two isopropyl methyl doublets, and this is presumably because the methyl groups of the β-diiminato backbone CH(C(*Me*)N-2,6-${}^iPr_2C_6H_3)_2$ hinder rotation in relation to the less sterically demanding CH group of the Schiff bases **C** and **D**.

Complexes **II** and **IV**, which contain four-coordinate zinc(II) ions, are chiral. In these instances there are four sets of isopropyl doublets in the low-temperature spectra of **II** and for the room-temperature spectrum of **IV**. Since the molecules have only C_2 symmetry, the isopropyl methyl groups are diastereotopic and we therefore should expect to see two doublets for the isopropyl methyl group even when rotation about the N−C(phenyl) bond is rapid. If this is frozen out, we may see four sets of doublets.

When the temperature is raised, the ${}^1H$ NMR spectra of **II** show that there is a pairwise coalescence of the isopropyl methine and methyl signals giving rise to one septet and two doublets at 50 °C. With further heating the latter start to broaden and approach coalescence at 100 °C. These changes are shown in Figure 4. At high temperatures we propose that we are observing the reversible dechelation of the Schiff base ligand as represented by eq 1. The dissociation of the Zn−N bond will generate a three-coordinate trigonal zinc(II) species which will be akin to complexes **I** and **III**. Thus, with free rotation about the N−C(phenyl) bond, we expect to see just one isopropyl doublet. This situation parallels that recently described

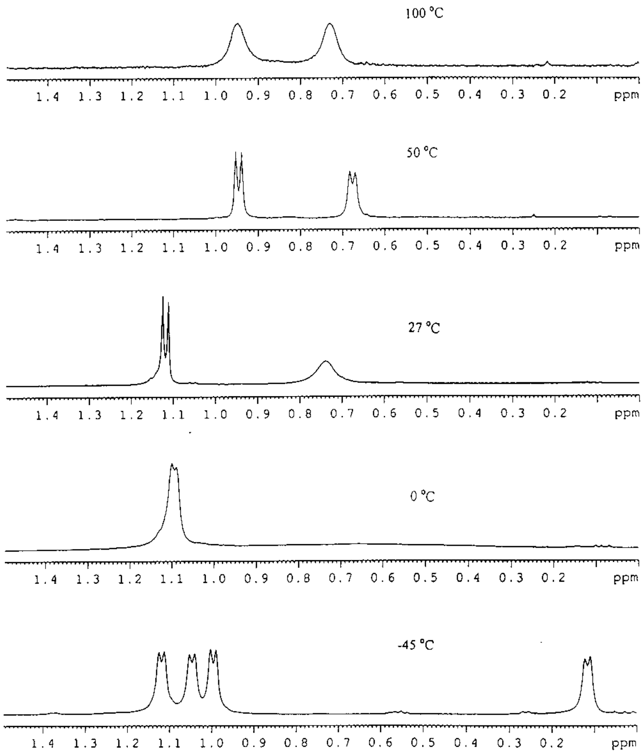

Figure 4. Variable-temperature ^{1}H NMR spectra of the methyl groups in compound **II** (in toluene-d_8).

for the BDI complex (BDI)Mg(O^{t}Bu)(THF) which reversibly dissociates THF in solution according to eq 2.[4] At low

$$\mathrm{Zn}(\eta^2\text{-}\overset{\frown}{\mathrm{O\;\;N}})_2 \rightleftharpoons \mathrm{Zn}(\eta^2\text{-}\overset{\frown}{\mathrm{O\;\;N}})\,(\eta^1\text{-}\overset{\frown}{\mathrm{O\;\;N}}) \qquad \text{eq. 1}$$

$$\mathrm{(BDI)Mg(O^tBu)(THF)} \rightleftharpoons \mathrm{(BDI)Mg(O^tBu)} + \mathrm{THF} \qquad \text{eq. 2}$$

temperatures, the BDI ligand shows four isopropyl methyl groups, but, when dissociation of THF occurs on increasing the temperature and the equilibrium shown in eq 2 is driven to the right, there are two isopropyl methyl groups. Again the difference between the Schiff base ligands and the BDI ligand can be attributed to the lack of rotation about the N−C(phenyl) bond in the latter, even at high temperatures.

Polymerization Studies. The focus of our attention has been the reactivity of the monomeric three-coordinate zinc amide and phenoxide compounds, **I** and **III**, respectively, as precursors for lactide and propylene oxide polymerization.

Both **I** and **III** were found to ring-open L-lactide to produce isotactic PLA in benzene at room temperature. Similarly, **I** and **III** catalyzed polymerization of *rac*-lactide to give atactic poly-*rac*-lactide. In our studies, the ratio of [lactide] to [Zn] was ca. 20:1 and polymerization occurred slowly at 25 °C proceeding to 90% conversion in ca. 3 h for **I** and ca. 72 h for **III**. The difference in reactivity between those two compounds can be traced to the rate of initiation which is notably slower for the bulky 2,6-*tert*-butylphenoxide. The lack of stereoselectivity in the polymerization of *rac*-lactide by **I** and **III** when compared to the polymerization induced by [(BDI)Zn(O^{i}Pr)][2b] presumably reflects the less sterically hindered metal center when coordinated by the Schiff base ligand L_C relative to its β-diiminato counterpart, BDI.

Compounds **I** and **III** showed no reactivity toward ring-opening of propylene oxide at room temperature, nor did we observe any copolymerization in attempted reactions employing PO and CO_2 under ambient conditions. Upon heating compounds **I** and **III** in solution to 50 °C and above, ligand scrambling was observed yielding $(L_C)_2Zn$ (**IV**) along with either $Zn(NSi_2Me_6)_2$ or $Zn(OC_6H_3\text{-}2,6\text{-}^tBu_2)_2$. The occurrence of this Schlenk equilibrium precludes the use of **I** and **III** as single-site catalysts for ROP of epoxides and copolymerization of epoxides with CO_2. The formation of $Zn(OAr')_2$ effectively yields a catalyst system analogous to that employed by Darensbourg *et al.*[1] The bis-Schiff base complexes, **II** and **IV**, are inactive for ROP of PO and lactides, at least under mild conditions.

Concluding Remarks

The use of the sterically demanding Schiff base ligand shown in **C** has allowed the preparation of the three-coordinate monomeric zinc amide and phenoxide complexes **I** and **III**. These compounds are, however, thermally sensitive to ligand scrambling upon heating both in the solid state and in solution. While lactide polymerization can be initiated, the ring-opening of PO is not seen. There is now increasing evidence to support the view that ROP of lactides may be achieved at a single metal center, but ROP of PO has not been documented to occur in a similar manner. Only strong Lewis acidic metal centers are known to initiate cationic type polymerization of PO, which gives regioirregular PPO, unlike base catalysis, which generates regioregular (HTHTHT) triads.[5] The present work is, however, of interest in comparison to the (BDI)Zn systems developed by Coates and co-workers[2] in revealing the importance of the greater steric demands of the BDI ligands.

Acknowledgment. We thank Dr. Karl Vermillion for his help with the variable-temperature NMR experiments.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010560E