Synthesis and Structures of (Dialkylamino)ethylcyclopentadienyl Derivatives of Zinc

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Lithium salts of (dialkylamino)ethylcyclopentadienyl react with either $ZnCl_2$ or $Zn(OAc)_2$ to afford dimeric derivatives containing bridging chlorides or acetates, respectively. X-ray structural determinations of three such derivatives show that the cyclopentadienyl ligands are bound to the zinc centers in an η^1 fashion and via their amine groups, thereby leading to a stable six-membered metallacycle.

Introduction

Transition metal derivatives of (dialkylamino)ethylcyclopentadienyl (DEC) ligands have been effectively employed as homogeneous catalysts for various processes.[1−3] For example, very active chromium catalysts containing this ligand system which operate at ambient temperature and low pressures have been reported.[4] Importantly, these catalysts require reduced quantities of the cocatalyst (methylaluminoxane) (MAO) compared to other metallocene-based catalyst systems. Because of our interest in efficiently catalyzing the copolymerization of epoxides and carbon dioxide to provide polycarbonates, we have synthesized dimeric DEC derivatives of zinc. These complexes are modeled after the very competent β-diimine complexes of zinc acetate and methoxide employed by Coates et al. for the copolymerization of cyclohexene oxide and CO_2.[5] Although cyclopentadienyl derivatives of zinc are rather uncommon, zincocenes possessing cyclopentadienyl ligands of varying electronic and steric properties have been synthesized and structurally shown to possess “slipped-sandwich” motifs containing both $^1\eta$- and $^5\eta$-cyclopentadienyl ligands.[6−9] ^{1}H NMR spectra of these derivatives in solution reveal rapid haptotropic exchange between η^1- and η^5-coordination. In addition (cyclopentadienyl)(methyl)zinc is monomeric in the gas phase, where the cyclopentadienyl ligand features η^5-coordination to zinc, thereby creating an 18-electron shell for the zinc atom. However, in the crystalline state chains with cyclopentadienyl ligands bridging zinc centers are formed. Hence, the nature of the binding between zinc and DEC ligands is intrinsically worthy of investigation.

Results and Discussion

The (dialkylamino)ethylcyclopentadienyl derivatives of zinc were synthesized via the addition of equimolar quantities of the respective lithiated ligand salt (prepared by reacting 1 equiv of the ligand with 1 equiv of ^{t}BuLi in Et_2O at −40 °C) to a THF slurry of $ZnCl_2$ or $Zn(OAc)_2$ (see Scheme 1). It is important to distill the DEC-H ligands, to remove any ethanol used in their synthesis, prior to carrying out the lithiation reaction (vide infra). The complexes(**1**−**3**) were isolated in purified yield >50% and recrystallized from a minimal amount of methylene chloride at −20 °C to provide crystals (**1** and **2**) suitable for X-ray analysis.

The solid-state structure of complex **1** consists of a planar arrangement of zinc and chlorine atoms, separated by an average distance of 2.3591(10) Å, which form a parallelogram with Cl−Zn−Cl and Zn−Cl−Zn bond angles of 86.92(3)° and 93.08(3)°, respectively. The remaining coordination sites about the zinc centers are occupied by the cyclopentadienyl ring bound in an $^1\eta$ fashion with a Zn−C bond distance of 2.063(3) Å and the amine arm of the cyclopentadienyl ligand with a Zn−N bond distance of 2.124(3) Å. This bidentate arrangement of the DEC ligand with zinc affords a stable six-membered metallacycle with a C−Zn−N bite angle of 108.70(13)°. The nonbonding zinc−zinc separation in complex **1** was determined to be 3.245 Å. Figure 1 contains a thermal ellipsoid drawings of complex **1**, with the corresponding representation of complex **2** depicted in Figure 2. Complex **2** exists as an *anti*−*syn*-bridged acetate dimer in the solid state with a Zn···Zn nonbonding distance of 3.821 Å. As observed in complex **1** the cyclopentadienyl ligand is bound via a single carbon atom and the appended pyrrolidyl group to zinc at bond distances of 2.110(2) and 2.172(2) Å, with a N−Zn−C bond angle of 106.72(8)°. These bond lengths are significantly longer than those found in complex **1**. The two bridging acetate ligands form an eight-membered metallacycle with two zinc centers. This

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10.1021/om010519j CCC: $20.00

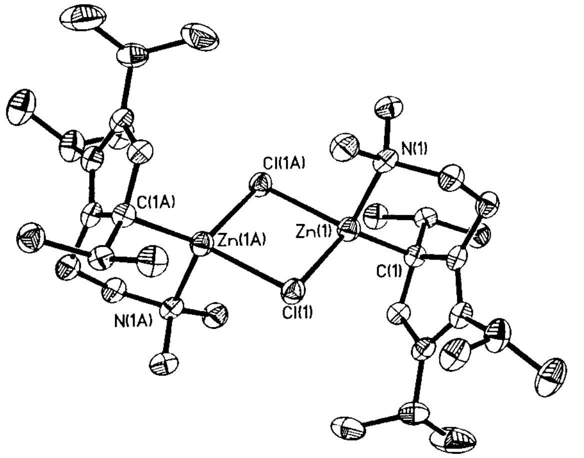


Figure 1. Thermal ellipsoid representation of $[(\eta^1\text{-}Me_2NC_2H_4C_5H^iPr_3)Zn(\mu\text{-}Cl)]_2$ (**1**).

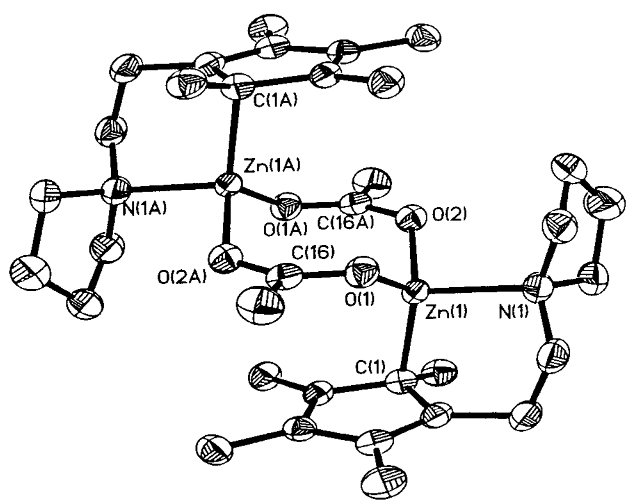


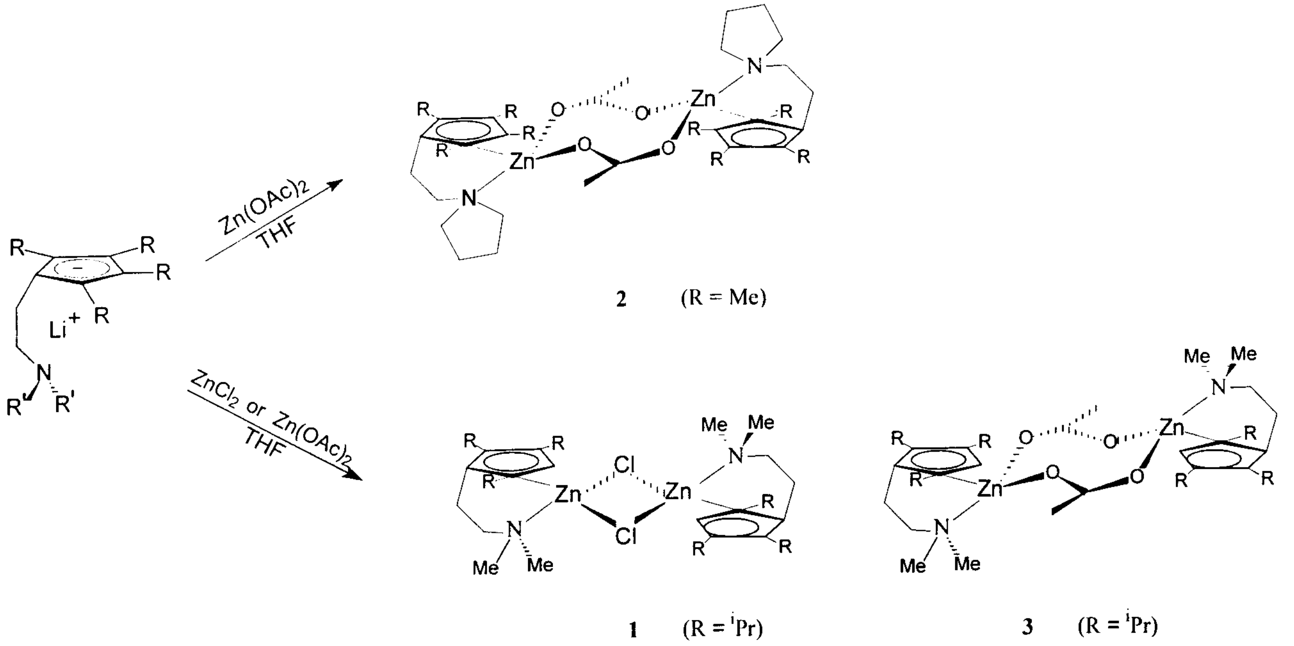
Figure 2. Thermal ellipsoid representation of $[(\eta^1\text{-}cyclo\text{-}C_4H_8NC_2H_4C_5Me_4)Zn(\mu\text{-}OAc)]_2$ (**2**).

anti–*syn* bonding mode of the acetates, with an average Zn–O bond distance of 1.970(2) Å and O–Zn–O bond angle of 113.97(8)°, leads to a chair conformation of this eight-membered metallacycle which minimizes steric interaction between the two (DEC)Zn moieties.

During our initial synthetic attempt at preparing complex **2** we employed a sample of DEC-H-**2** which was not purified by distillation. In this instance complex **4** was isolated and was shown by X-ray crystallography to contain two zinc centers asymmetrically bridged by acetate and ethoxide ligands (Figure 3). The ethoxide ligand presumably resulted from some remaining ethanol in the DEC-H ligand sample prior to deprotonation with ${}^tBuLi$. The solid-state structural details of complex **4** are reported here for completeness. Unlike the *anti*–*syn*-bridged acetate ligands in complex **2**, the acetate bridge in complex **4** exhibits a *syn*–*syn* geometry with a Zn···Zn distance of 3.397 Å. The average Zn–O bond distances for the acetate and ethoxy bridges were found to be 2.014(2) and 1.962(2) Å, respectively. The Zn–O–Zn bond angle of the ethoxy bridge was determined to be 119.94(12)°, and the O–C–O bond angle of the acetate bridge was found to be 125.3(3)°. The Zn–C and Zn–N bond distances of 2.125 and 2.158(3) Å to the chelated amino-cyclopentadienyl ligand are similar to those seen in complex **2**. Table 1 contains a compilation of select bond distances and bond angles in complexes **1**, **2**, and **4**.

The infrared spectrum of complex **2** in methylene chloride in the $\nu(CO_2)$ region is consistent with the dimeric structure observed in the solid state. That is, the solution and solid-state infrared spectra are quite similar (see Figure 4), where the asymmetric and symmetric $\nu(CO_2)$ vibrations occur at 1594 and 1437 cm^{-1}, and 1595 and 1435 cm^{-1}, respectively. Indeed, $\Delta\nu(CO_2)$ at 157 and 160 cm^{-1} is exactly what is anticipated for a bridging acetate ligand.[10] Upon adding 20 molar equiv of propylene oxide to a methylene chloride solution of **2**, there was *no* change in the $\nu(CO_2)$ infrared region, or in other words propylene oxide under these conditions

Scheme 1



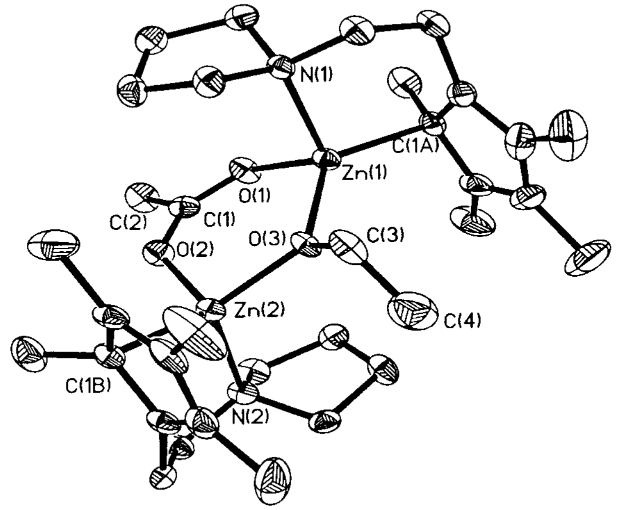


Figure 3. Thermal ellipsoid representation of $[(\eta^1\text{-cyclo-}C_4H_8NC_2H_4C_5Me_4)_2Zn(\mu\text{-OAc})(\mu\text{-OEt})]$ (**4**).

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 1, 2, and 4

	Complex **1**		
Zn(1)−Cl(1)	2.3332(10)	N(1)−Zn(1)−C(1)	108.70(13)
Zn(1)−N(1)	2.124(3)	N(1)−Zn(1)−Cl(1)	104.21(9)
Zn(1)−C(1)	2.063(3)	Cl(1)−Zn(1)−C(1)	123.77(10)
Zn(1)−Cl(1A)	2.3850(10)	Cl(1)−Zn(1)−Cl(1A)	93.08(3)
		C(1)−Zn(1)−Cl(1A)	124.00(10)
		N(1)−Zn(1)−Cl(1A)	99.14(8)
	Complex **2**		
Zn(1)−O(1)	1.9635(16)	O(1)−Zn(1)−O(2)	113.97(8)
Zn(1)−O(2)	1.9779(15)	C(1)−Zn(1)−N(1)	106.72(8)
Zn(1)−C(1)	2.110(2)	N(1)−Zn(1)−O(2)	103.26(8)
Zn(1)−N(1)	2.1271(19)	N(1)−Zn(1)−O(1)	97.06(7)
		O(1)−Zn(1)−C(1)	122.71(8)
		O(2)−Zn(1)−C(1)	110.03(7)
	Complex **4**		
Zn(1)−O(3)	1.964(2)	Zn(2)−O(3)	1.959(2)
Zn(1)−O(1)	2.005(2)	Zn(2)−O(2)	2.023(2)
Zn(1)−C(1A)	2.125(3)	Zn(2)−C(1B)	2.109(3)
Zn(1)−N(1)	2.158(3)	Zn(2)−N(2)	2.127(13)
O(3)−Zn(1)−O(1)	103.38(9)	O(3)−Zn(2)−O(2)	102.12(9)
O(3)−Zn(1)−C(1A)	130.95(12)	O(3)−Zn(2)−C(1B)	128.91(11)
O(1)−Zn(1)−C(1A)	104.63(12)	O(2)−Zn(2)−C(1B)	106.86(11)
O(3)−Zn(1)−N(1)	105.74(9)	O(3)−Zn(2)−N(2)	114.8(3)
O(1)−Zn(1)−N(1)	103.33(10)	O(2)−Zn(2)−N(2)	94.3(3)
C(1A)−Zn(1)−N(1)	105.87(12)	C(1B)−Zn(2)−N(2)	104.0(2)

did not disrupt the zinc dimer. However, in pure propylene oxide solution the dimer is partially severed, as seen by the appearance of an additional $\nu(CO_2)$ infrared absorption at 1610 cm^{-1} ascribed to the asymmetric $\nu(CO_2)$ stretch of a terminal acetate ligand. By way of contrast complex **3** when dissolved in methylene chloride solution, on the basis of $\nu(CO_2)$ infrared spectroscopy, appears to exist as both monomer and dimer in solution, presumably due to the more sterically demanding isopropyl substituents of the cyclopentadienyl ligand.

We have examined the use of these complexes for the copolymerization of CO_2 with both propylene oxide and cyclohexene oxide. Unfortunately, all three complexes (**1**−**3**) exhibited poor reactivities for the copolymerization process, ranging from 1.2 to 2.1 g polymer/g Zn/h for reaction conditions of 30 °C and 600 psi of CO_2. Furthermore, the polymers produced by these systems had a large content(~15−20 mol %) of polyether linkages. Increasing the reaction temperature to 80 °C led only to a small increase in catalytic activity (2.5 g polymer/g Zn/h) with an even greater percentage of polyether linkages. Independent experiments showed these complexes were easily decomposed under the conditions of catalysis, accounting for the low catalytic activity. Because the catalysts were found to decompose under both low (30 °C) and high (80 °C) reaction conditions, it does not appear to be a simple thermal decomposition process. It is tempting to speculate that CO_2 insertion into the Zn−C bond, a process highly dependent on CO_2 pressure,[11] with concomitant C−C bond formation may be responsible for the instability of these complexes. Although the zinc derivatives have been shown to be ineffective as catalysts for the copolymerization of CO_2/epoxides, these complexes represent a novel group of well-characterized cyclopentadienyl derivatives of a group 12 metal. Comparative studies of the cadmium analogues that may display an alternative mode of binding to the cyclopentadienyl ligand are underway.

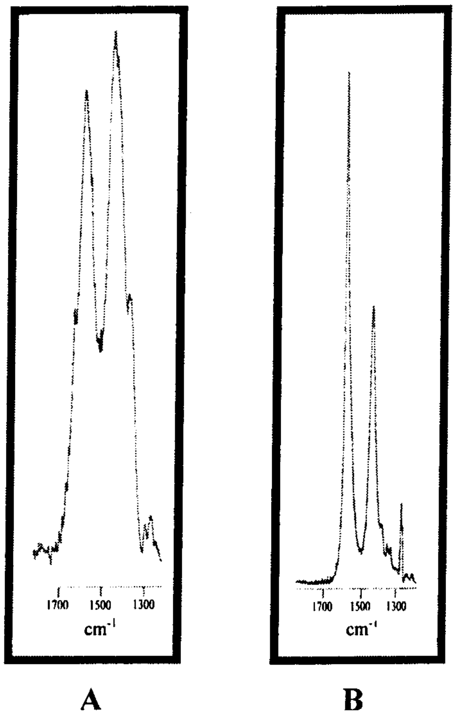


Figure 4. Infrared spectrum of $[(\eta^1\text{-cyclo-}C_4H_8NC_2H_4C_5Me_4)Zn(\mu\text{-OAc})]_2$ (**2**): (A) in KBr; (B) in methylene chloride solution.

Experimental Section

Methods and Materials. Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. Glassware was flamed out thoroughly prior to use. Solvents were freshly distilled from sodium benzophenone before use. Cyclohexene oxide and propylene oxide were purchased from Aldrich Chemical Co. and purified by distillation over calcium hydride. Bone dry

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carbon dioxide was purchased from Scott Specialty Gases, Inc. Zinc chloride and zinc acetate were purchased from Aldrich Chemical Co. and stored in a glovebox prior to use. The *tert*-butyllithium (1.7 M in hexane) was also purchased from Aldrich and placed in the refrigerator. Both the $[\mathrm{Me_2NC_2H_4C_5H_2{}^iPr_3}]$ (DEC-H-**1**) and $[\mathrm{cyclo\text{-}C_4H_8NC_2H_4C_5Me_4H}]$ (DEC-H-**2**) were obtained from DSM Research in Geleen, The Netherlands, and were distilled prior to use. Synthesis of the $[\mathrm{Me_2NC_2H_4C_5H_2{}^iPr_3}]$ ligand is accomplished according to the methods of Rausch and co-workers,[12] and the synthesis of $[\mathrm{cyclo\text{-}C_4H_8NC_2H_4C_5Me_4H}]$ is achieved through the route described in the literature.[4] The synthesis of the lithium ligand salts are reported herein. Infrared spectra were recorded on a Mattson 6081 spectrometer with DTGS and mercury cadmium telluride (MCT) detectors. All isotopically labeled solvents for NMR experiments were purchased from Cambridge Isotope Laboratories. ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-200E, Unity +300 MHz, and VXR 300 MHz superconducting high-resolution spectrometers.

Synthesis of $(\mathbf{Me_2NC_2H_4C_5H^iPr_3})$Li and $(\mathbf{cyclo\text{-}C_4H_8NC_2H_4C_5Me_4})$Li. A solution of 3.35 mL of ^{t}BuLi (1.7 M in hexanes) was added dropwise to 1.50 g of $[\mathrm{Me_2NC_2H_4C_5H_2{}^iPr_3}]$ or 1.25 g of $[\mathrm{cyclo\text{-}C_4H_8NC_2H_4C_5Me_4}]$ in 30 mL of ether at −40 °C. After the ^{t}BuLi reagent was added, the resulting solution was allowed to warm to room temperature and stirred for 1 h. The ether solvent was removed by vacuum, and the white solid salt was washed with pentane, whereby any remaining free ligand was extracted. The respective yields for the lithium salts were 1.09 g (70%) for the $(\mathrm{Me_2NC_2H_4C_5H^iPr_3})\mathrm{Li}$ and 0.90 g (66%) for the $(\mathrm{cyclo\text{-}C_4H_8NC_2H_4C_5Me_4})\mathrm{Li}$.

Synthesis of $[(\eta^1\text{-}\mathbf{Me_2NC_2H_4C_5H^iPr_3})\mathbf{Zn}(\mu\text{-}\mathbf{Cl})]_2$ (1). A 5 mL THF solution of $(\mathrm{Me_2NC_2H_4C_5H^iPr_3})\mathrm{Li}$ (0.20 g, 0.74 mmol) was added to 5 mL of a THF slurry of $\mathrm{ZnCl_2}$ (0.10 g, 0.74 mmol), resulting in a clear light yellow solution, which was stirred at ambient temperature for 24 h. The THF solvent was removed by vacuum, leaving a light tan powder. The solid was then dissolved in methylene chloride, leaving the LiCl salt insoluble for filtration. The methylene chloride solution was then concentrated to 3 mL and placed in a refrigerator at −20 °C. Colorless block crystals formed after several days. The supernate was transferred off by cannula and crystals dried under vacuum to yield 0.18 g of product (68%). Anal. Calcd for $\mathrm{C_{36}H_{66}N_2Cl_2Zn_2}$: C, 59.34; H, 9.13. Found: C, 58.30; H, 8.92. ^{1}H NMR ($\mathrm{CD_3CN}$): 1.04 [d, 24H{3,5-CHMe_3}], 1.19 [d, 12H{2-CHMe_3}], 2.18 [s, 12H{NMe_2}], 2.40 [m, 4H{N−CH_2−}], 2.69 [s, 4H{N−CH$_2$CH_2−}], 2.81 [septet, 4H{3,5-CHMe$_2$}], 3.07 [septet, 2H{2-CHMe$_2$}], 5.43 [s, 2H{Cp−H}]. ^{13}C{H} NMR ($\mathrm{CD_3CN}$): 24.06−45.35{CH$_2$, CH$_3$}, 54.12−62.18{N−CH$_2$}, 124.65−146.12{C, Cp ring}.

Synthesis of $[(\eta^1\text{-}\mathbf{cyclo\text{-}C_4H_8NC_2H_4C_5Me_4})\mathbf{Zn}(\mu\text{-}\mathbf{OAc})]_2$, (2). A 5 mL THF solution of $(\mathrm{cyclo\text{-}C_4H_8NC_2H_4C_5Me_4})\mathrm{Li}$ (0.20 g, 0.89 mmol) was added to 5 mL of a THF slurry of $\mathrm{Zn(OAc)_2}$ (0.17 g, 0.89 mmol), resulting in a clear light yellow solution, which was stirred at room temperature for 24 h. The THF solvent was removed under vacuum, leaving a tan powder. The solid was then dissolved in methylene chloride, leaving the LiCl salt for filtration. The methylene chloride solution was then concentrated to 3 mL and placed in a refrigerator at −20 °C. Colorless block crystals formed after several days. The supernate was transferred off by cannula, and crystals were dried under vacuum to yield 0.165 g of product (54%). Anal. Calcd for $\mathrm{C_{34}H_{54}N_2O_4Zn_2}$: C, 59.56; H, 7.94. Found: C, 59.80; H, 7.86. ^{1}H NMR ($\mathrm{CD_3CN}$): 1.68 [m, 16H{C$_2$H$_4$}], 1.71−1.80 [(4)s, 24H{CpMe_4}], 1.89 [s, 6H{O$_2$CCH_3}], 2.36 [s, 4H{N−CH$_2$−CH_2}], 2.42−2.62 [m, 12H{NCH_2}]. ^{13}C{H} NMR ($\mathrm{CD_3CN}$): 11.65−14.95{Cp−CH$_3$}, 19.34{O$_2$CCH$_3$}, 24.62−27.91{CH$_2$}, 50.87−57.95{N−CH$_2$}, 134.84−142.04{C, Cp ring}, 176.32{O$_2$$CCH_3$}.

Synthesis of $[(\eta^1\text{-}\mathbf{Me_2NC_2H_4C_5H^iPr_3})\mathbf{Zn}(\mu\text{-}\mathbf{OAc})]_2$ (3). A 5 mL THF solution of $(\mathrm{Me_2NC_2H_4C_5H^iPr_3})\mathrm{Li}$ (0.200 g, 0.74 mmol) was added to a 5 mL THF slurry of $\mathrm{Zn(OAc)_2}$ (0.136 g, 0.74 mmol), resulting in a clear light yellow solution, which was stirred at room temperature for 24 h. The suspension was filtered over a frit, and the THF solvent was removed by vacuum, leaving a deep yellow sticky residue behind. The residue was then dissolved in methylene chloride and was consequently concentrated to 3 mL and placed in a refrigerator at −20 °C. Unfortunately suitable crystals for X-ray analysis were not obtained. Anal. Calcd for $\mathrm{C_{40}H_{72}N_2O_4Zn_2}$: C, 61.93; H, 9.35. Found: C, 61.10; H, 8.96. ^{1}H NMR ($\mathrm{CD_3CN}$): 1.06 [d, 24H{3,5-CHMe_3}], 1.19 [d, 12H{2-CHMe_3}], 1.86 [s, 3H{O$_2$CCH_3}] 2.31 [s, 12H{NMe_2}], 2.37 [m, 4H{ N−CH$_2$CH_2−}], 2.70 [s, 4H{ N−CH_2−}], 2.83 [septet, 4H{3,5-CHMe$_2$}], 3.06 [septet, 2H{2-CHMe$_2$}], 5.44 [s, 2H{Cp-H}]. ^{13}C{H} NMR ($\mathrm{CD_3CN}$): 19.51{O$_2$CCH$_3$}, 23.27−46.15{CH$_2$, CH$_3$}, 55.77−61.80-{N−CH$_2$}, 124.73−146.53{C, Cp ring}, 177.45{O$_2$$CCH_3$}.

Synthesis of $[(\eta^1\text{-}\mathbf{cyclo\text{-}C_4H_8NC_2H_4C_5Me_4})_2\mathbf{Zn_2}(\mu\text{-}\mathbf{OAc})(\mu\text{-}\mathbf{OEt})]$ (4). A 0.20 g sample containing 50/50 mol % composition of LiOEt and of $(\mathrm{cyclo\text{-}C_4H_8NC_2H_4C_5Me\ })\mathrm{Li}$ (0.89 mmol) was added to a 5 mL THF slurry of $\mathrm{Zn(OAc)_2}$ (0.17 g, 0.89 mmol), resulting in a clear light yellow solution, which was stirred at room temperature for 24 h. The THF solvent was removed by vacuum, leaving a tan powder. The solid was then dissolved in methylene chloride, leaving the LiCl salt for filtration. The methylene chloride solution was then concentrated to 3 mL and placed in a refrigerator at −20 °C. Colorless block crystals formed after several days. The supernate was transferred off by cannula, and crystals were dried under vacuum to yield 0.18 g of product (68%). ^{1}H NMR ($\mathrm{CD_3CN}$): 1.06 [m, 16H{C$_2$H$_4$}], 1.66−1.80 [(4)s, 24H{CpMe_4}], 1.89 [s, 6H{O$_2$CCH_3}], 1.95 [s, 4H{CH_2}], 2.42 [m, 4H{NCH_2}], 2.37 [m, 4H{N−CH_2−}, 2.45 [m, 8H{N−(CH)$_2$−}], 3.64 [t, OCH$_2$-CH$_3$}]. ^{13}C{H} NMR ($\mathrm{CD_3CN}$): 11.72−14.89{Cp-CH$_3$}, 17.32-{O−CH$_2$$CH_3$}, 19.01{O$_2CCH_3$}, 24.75−27.83{$CH_2$}, 49.56−58.65{N−$CH_2$, O−$CH_2CH_3$}, 134.67−141.82{$C$, Cp ring}, 176.78{O$_2$$CCH_3$}.

X-ray Crystallography. A Bausch and Lomb 10× microscope was used to identify suitable colorless crystals of **1**, **2**, and **4** from a representative sample of crystals of the same habit. The representative crystal was coated in a cryogenic protectant (i.e., mineral oil, paratone, or apezeon grease) and was then fixed to a glass fiber, which in turn was fashioned to a copper mounting pin. The mounted crystals were then placed in a cold nitrogen stream (Oxford) maintained at 110 K on a Bruker SMART 1000 three-circle goniometer.

Crystal data and details of data collection for the complexes are provided in Table 2. The X-ray data were collected on a Bruker CCD diffractometer and covered more than a hemisphere of reciprocal space by a combination of three sets of exposures; each exposure set had a different φ angle for the crystal orientation and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.9 cm. Crystal decay was monitored by repeating the data collection for 50 initial frames at the end of the data set and analyzing the duplicate reflections; crystal decay was negligible. The space group was determined on the basis of systematic absences and intensity statistics.[13]

The structures were solved by direct methods. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R(F)$ and $wR(F^2)$ values, as indicated in Table 2 at convergence. Hydrogen atoms were place in idealized positions with isotropic thermal parameters fixed 1.2 or 1.5 times the value of the attached atom. Neutral atom scattering factors and anomalous scattering factors were taken from the International Tables for X-ray Crystallography, Vol. C.

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[12] Flores, J.; Chien, J.; Rausch, M. *Organometallics* **1994**, *13*, 4140.

[13] *SMART* 1000 CCD; Bruker Analytical X-ray Systems: Madison, WI, 1999.

Table 2. Crystallographic Data for Complexes 1, 2, and 4

	1	**2**	**4**
empirical formula	$C_{36}H_{66}N_2Cl_2Zn_2$	$C_{34}H_{54}O_4N_2Zn_2$	$C_{34}H_{56}O_3N_2Zn_2$
fw	728.71	685.66	671.68
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	*Pbca*	*P*2(1)/*n*
V, Å^3	958.9(3)	3385.2(3)	3366.9(9)
Z	2	6	6
a, Å	8.5668(14)	11.5547(6)	11.0009(18)
b, Å	9.9256(16)	14.6242(8)	19.208(3)
c, Å	12.1500(19)	20.0334(10)	16.249(3)
α, deg	100.348(3)	—	—
β, deg	99.679(3)	—	101.295(3)
γ, deg	104.521(3)	—	—
T, K	110(2)	110(2)	110(2)
d(calcd), g/cm^3	1.307	1.613	1.975
abs coeff, mm^{-1}	1.419	2.161	2.188
R,[a] % [$I > 2\sigma(I)$]	6.03	5.61	4.74
R_w,[a] %	14.98	16.94	9.64

[a] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$. $Rw = \{[\Sigma w(F_o^2 - F_c^2)^2/[\Sigma w(F_o^2)^2]\}^{1/2}$.

For the title compound, data reduction: SAINTPLUS (Bruker[14]); program(s) used to solve the structure: SHELXS-86 (Sheldrick[15]); program(s) used to refine the structure: SHELXL-97 (Sheldrick[16]); program(s) used for molecular graphics: SHELXTL version 5.0 (Bruker[17]); software used to prepare material for publication: SHELXTL version 5.0 (Bruker[17]).

High-Pressure Copolymerization of CO_2 with Cyclohexene Oxide. A sample of the active catalyst (0.100 g) was dissolved in 20.0 mL of cyclohexene oxide. The solution was loaded via an injection port into a 300 mL stainless steel Parr autoclave, which had previously been dried overnight under vacuum at 80 °C. The reactor was pressurized to 600 psi with CO_2 and heated to 30−80 °C, which increased the pressure to 600−1020 psi, and allowed to react for 24−48 h. After 24−48 h of reaction time, the reactor was cooled and opened and the viscous/solid mixture isolated by dissolution in CH_2Cl_2 and precipitated out in MeOH. The polymer was analyzed by ^{1}H and ^{13}C NMR spectroscopy. Several trials were performed to gauge the effects of varying temperature on the activity of the catalysts.

High-Pressure Copolymerization of CO_2 with Propylene Oxide. A 0.100 g amount of active catalyst was dissolved in 20.0 mL of propylene oxide. The resulting solution was added through the injection port to a predried 300 mL autoclave, and the reactor was pressurized to 600 psi with CO_2. The reactor was heated at 55 °C, raising the pressure to 650−700 psi, for 48 h. After this period of time, the reaction mixture was diluted with CH_2Cl_2 (1:10) and analyzed by infrared spectroscopy in the $\nu(CO_2)$ region.

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Supporting Information Available: Fully labeled diagrams and tables of crystallographic data, data collection, solution and refinement details, positional and thermal parameters, and tables of bond distances/bond angles of **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Bruker. *SAINT-Plus*, version 6.02; Madison, WI, 1999.

(15) Sheldrick, G. *SHELXS-86*, Program for Crystal Structure Solution; Institut fur Anorganische Chemie der Universitat, Tammanstrasse 4, D-3400 Gottingen, Germany. 1986.

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(17) Bruker. *SHELXTL*, version 5.0; Madison, WI, 1999.