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Mechanistic Aspects of the Copolymerization of CO_2 and Epoxides by Soluble Zinc Bis(phenoxide) Catalysts as Revealed by Their Cadmium Analogues

D. J. Darensbourg,* S. A. Niezgoda, J. D. Draper, and J. H. Reibenspies

Contribution from the Department of Chemistry, Texas A&M University, P.O. Box 300012,
College Station, Texas 77842

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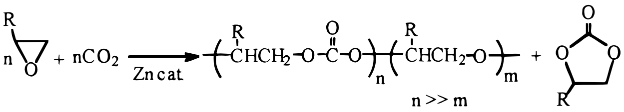
Abstract: A family of monomeric cadmium(II) phenoxides of the general formula $Cd(O\text{-}2,6\text{-}R_2C_6H_3)_2(base)_{2-3}$ [R = Ph, ^tBu, Me; base = THF, THT, pyridine, propylene carbonate] has been synthesized. Determination of the solid-state structures of all complexes have uncovered a variety of geometries ranging from the expected distorted tetrahedral to square planar to trigonal bipyramidal, depending upon the identity of the phenoxide substituents and of the base ligands. By utilizing multinuclear NMR techniques available to cadmium, particularly ^{113}Cd NMR, it was possible to discover the identities of these complexes in solution. Reactivities of these complexes with the small molecules CO_2, COS, and CS_2 were also carried out. While CO_2 showed no reactivity with the sterically encumbered Cd(II) bis(phenoxides), insertion was observed spectroscopically to occur for COS and CS_2. The product of CS_2 insertion was isolated and characterized and found to be a dimeric xanthate complex, $[Cd(S_2CO\text{-}2,6\text{-}Ph_2C_6H_3)]_2[\mu\text{-}O\text{-}2,6\text{-}Ph_2C_6H_3]_2$. These Cd(II) complexes are analogues to Zn(II) bis(phenoxides), which are highly active catalysts for the copolymerization of CO_2 with epoxides. Although the Cd(II) bis(phenoxides) show only greatly reduced activity for this copolymerization reaction, the results of solution studies and reactivities have proven instructive toward better understanding the mechanism through which their Zn(II) counterparts work.

We have recently discovered that monomeric bis(phenoxides) of zinc, $Zn(O\text{-}2,6\text{-}R_2C_6H_3)_2(ether)_2$ [R = Ph, ^tBu, ^iPr, Me; ether = THF, diethyl ether], are excellent homogeneous catalysts for the copolymerization and terpolymerization of CO_2 with epoxides (eq 1).[1] These bis(phenoxide) zinc complexes are monomeric and hence soluble in many organic solvents and epoxides due to the use of the bulky substituents in the ortho positions of the phenoxide ligands which prevent aggregation.[2] High-molecular-weight copolymer can be obtained in moderate to extremely good yields, depending upon the catalyst derivative which is used. It has been possible to obtain full structural characterization of all of these catalyst derivatives to determine that all have roughly the same distorted-tertrahedral geometry in the solid state.[3] However, because of the absence of spectroscopic tools employable for zinc complexes, it has been difficult to elucidate the solution behavior of these complexes pertinent to understanding the mechanism through which they act and thus grasp the keys to optimization of the copolymerization process.



(1)

A general mechanism for the copolymerization process has been proposed for zinc catalysts which have at least one anionic oxygen-coordinating ligand, such as a carboxylate, an alkoxide, or a phenoxide.[4] As drawn in the skeletal mechanism in Scheme 1, initiation is believed to occur by coordination of the epoxide to the electrophilic Zn center. The coordinated epoxide is ring-opened through nucleophilic attack on the α-carbon by the oxygen ligand, leading to an alkoxide species which can then rapidly insert CO_2. The propagation of this polymer chain follows as the carbonate species can subsequently ring-open the next coordinated epoxide, followed again by CO_2 insertion. Although we have illustrated in Scheme 1 that ring opening occurs exclusively at the unsubstituted carbon center of the epoxide, it has been demonstrated by NMR experiments that ring opening takes place at either carbon atom.[5]

To uncover experimental evidence consistent or inconsistent with this mechanism for the Zn bis(phenoxide) catalyst system, we have again turned to the use of cadmium analogues. The use of cadmium(II) provides an accessible metal nucleus, ^{113}Cd, to more intimately examine the interaction and reactivity of the ligands at the metal center through multinuclear NMR techniques. Previously, we have been able to utilize Cd(II) carboxylate model complexes which contained a coordinated epoxide ligand to study the interaction of the epoxide with the metal center and the ring opening of the coordinated epoxide by the carboxylate ligand.[6]

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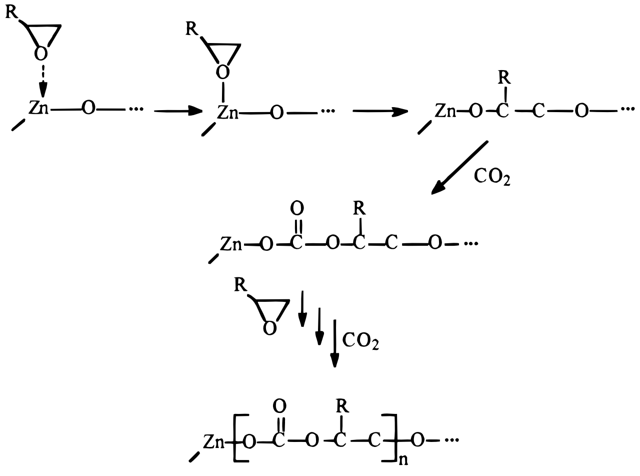
Scheme 1



Herein, we have synthesized a family of Cd(II) bis(phenoxides) analogous to our zinc catalysts. The solid-state structures of these complexes of the general formula $Cd(O\text{-}2,6\text{-}R_2C_6H_3)_2(solvent)_{2-3}$ adopt a variety of solid-state conformations, depending on the identity of the phenoxy substituents and the coordinating base. One derivative, $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2(THF)_2$ (**1**), previously reported by Buhro,[7] had an unexpected square-planar ligand arrangement which is considerably different from its tetrahedral zinc analogue. Recently, we have reported the structures of three more complexes of this family which each took on a different solid-state geometry: $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2(THT)_2$ (**2**) is another square-planar complex, $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2(py)_3$ (**3**) is trigonal bypyramidal, and $Cd(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THF)_2$ (**4**) has distorted tetrahedral geometry.[8] The syntheses and X-ray crystal structures of these and three more derivatives are reported here, including the results of structural redetermination of Buhro's complex carried out at low temperature. Nevertheless, it is important to note that all structural parameters in complex **1** determined at 193 K are quite similar to those previously reported at ambient temperature. Additionally, the results of solution ^1H, ^{13}C, and ^{113}Cd NMR experiments to determine the identity of these species in solution and to study the catalytic activity of these Cd(II) complexes are provided. In particular, reactions with the small molecules CO_2, COS, and CS_2 were carried out and a novel xanthate product formed from CS_2 insertion has been isolated and characterized.

Experimental Section

Methods and Materials. All complexes are extremely air- and moisture-sensitive and were handled using Schlenk and glovebox techniques under an argon atmosphere. Solvents were freshly distilled before use except for tetrahydrothiophene (THT) and pyridine, which were distilled over calcium hydride and stored over molecular sieves. Phenols and propylene carbonate were purchased from Aldrich and used as received. $Cd[N(SiMe_3)_2]_2$ was synthesized and distilled according to the literature procedure.[9] All isotopically labeled chemicals for NMR experiments were purchased from Cambridge Isotope Laboratories. Benzene-d_6 was distilled over calcium hydride and stored in the glovebox over molecular sieves. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL-200E superconducting high-resolution spectrometer. ^{113}Cd NMR spectra were recorded on a Varian XL-400E superconducting high-resolution spectrometer operating at 88 MHz using an external 0.1 M $Cd(ClO_4)_2/D_2O$ reference. Elemental analysis were carried out by Canadian Microanalytical Services, Ltd.

Synthesis of $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2(THF)_2$ (1). Synthesis was carried out in a manner similiar to the published procedure.[6] $Cd[N(SiMe_3)_2]_2$ (0.48 g, 1.11 mmol) in 2 mL of THF was stirred with a solution of 2,6-di-*tert*-butylphenol (0.458 g, 2.22 mmol) in 2 mL of THF. After the yellow solution was stirred for 2 h, the flask was placed at −20 °C. Colorless crystals formed overnight. The supernate was cannulated to a clean flask, and a second crop of crystals were isolated. With both yields, after removal of the supernate, the crystals were washed quickly with very cold THF and dried briefly under vacuum. The combined yields totaled 0.327 g (44%) of pale yellow crystalline solid. Anal. Calcd for $C_{36}H_{58}O_4Cd$: C, 64.8; H, 8.76. Found: C, 63.19; H, 8.51. ^1H NMR (C_6D_6): δ 1.25 [m, 4H, {THF}], 1.60 [s, 18H, {−CMe$_3$}], 3.48 [m, 4H, {THF}], 6.78 [t, 1H, {4-H}], 7.28 [d, 2H, {3,5-H}].

Synthesis of $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2(THT)_2$ (2). $Cd[N(SiMe_3)_2]_2$ (0.20 g, 0.46 mmol) in 1 mL of THT was stirred while 2,6-di-*tert*-butylphenol (0.19 g, 0.92 mmol) in 1 mL of THT was added. The resulting yellow solution was stirred for 2 h, then placed at −20 °C for 2 days while crystals of the product formed. The supernate was removed from the crystals by cannula, and the crystals were dried in vacuo to give 0.246 g (76%) of a yellow crystalline solid. Anal. Calcd for $C_{36}H_{58}O_4Cd$: C, 61.83; H, 8.36. Found: C, 60.47; H, 8.24. ^1H NMR (C_6D_6): δ 1.38 [4H, m, {THT}], 1.66 [18H, s, −^{t}Bu$_2$}], 2.47 [4H, m, {THT}], 6.8 [1H, t, {4-C_6H_3}], 7.3 [2H, d, {3,5-C_6H_3}].

Synthesis of $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2(pyridine)_3$ (3). A 2-mL pyridine solution of 2,6-di-*tert*-butylphenol (0.19 g, 0.92 mmol) was added to a solution of $Cd[N(SiMe_3)_2]_2$ (0.20 g, 0.46 mmol) in 2 mL of pyridine. After stirring for 1 h, the yellow solution was placed at −20 °C for 2 days. Pale yellow crystals formed and were isolated by removing the supernate, washing quickly with cold fresh pyridine and drying under vacuum to give 0.250 g (71%) of a yellow crystalline solid. Crystals suitable for X-ray diffraction were grown by dissolving the yellow crystals in toluene after removing the supernate and storing at −20 °C for 2 days. Anal. Calcd for $C_{43}H_{57}O_2N_3Cd$: C, 67.0; H, 7.69; N, 5.53. Found: C, 66.41; H, 7.48; N, 5.76. ^1H NMR (C_6D_6): δ 1.66 [18H, s, {-C-^{t}*Bu*}], 6.58 [3H, t, {C_5H_5N}], 6.88 [2H, t, {*p*-C_6H_3}], 6.9 [6H, t, {C_5H_5N}], 7.42 [4H, d, {*m*-C_6H_3}], 8.53 [6H, d, {C_5H_5N}]. $^{13}C\{H\}$ NMR (C_6D_6): δ 31.7 {−C*Me*$_3$}, 35.9 {−*C*Me$_3$}, 114.5 {4-C_6H_3}, 124.3 {C_5H_5N}, 125.3 {3,5-C_6H_3}, 134.0 {C_5H_5N}, 139.0 {2,6-C_6H_3}, 150.4 {C_5H_5N}, 168.5 {*ipso*-C_6H_3}.

Synthesis of $Cd(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THF)_2$ (4). 2,6-Diphenylphenol (0.455 g, 1.86 mmol) was dissolved in 4 mL of THF and added to a solution of $Cd[N(SiMe_3)_2]_2$ (0.40 g, 0.92 mmol) in 2 mL of THF. The pale yellow solution stirred for 3 h at room temperature, then was concentrated to less than 1 mL and placed at −20 °C. After 2−3 days, colorless crystals formed. They were isolated by removing the supernate and drying briefly under vacuum to give a yield of 0.360 g (52%) of pale yellow powder. The crystals may be washed with very cold THF to remove reaction byproducts, although the yield is variably reduced due to the high solubility of **2** in THF. Anal. Calcd for $C_{44}H_{42}O_4$: C, 70.73; H, 5.67. Found: C, 68.79; H, 5.50. ^1H NMR (C_6D_6): δ 6.8−7.3 (br, 13H, 2,6-$Ph_2C_6H_3$-), 3.59 (m, 4H, THF), 1.43 (m, 4H, THF). $^{13}C\{H\}$ NMR (C_6D_6): δ 168.1 {*ipso*-C_6O}, 125−132 {2,6-Ph_2C_6}, 67.9 {THF}, 25.9 {THF}.

Synthesis of $Cd(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THT)_2$ (5). A 3-mL THT solution of 2,6-diphenylphenol (0.228 g, 0.93 mmol) was added to a neat sample of $Cd[N(SiMe_3)_2]_2$ (0.20 g, 0.46 mmol), and the resulting pale yellow solution was stirred for 1 h at room temperature. The solution was concentrated to approximately half-volume and placed at −20 °C for 2 days. Opaque crystals formed and were isolated by removing the supernatant solution and drying under vacuum for 20

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Table 1. Crystallographic Data for **1**−**6** and **8**

	1	**2**	**3**	**4**	**5**	**6**	**8**
formula	$C_{36}H_{58}CdO_4$	$C_{36}H_{58}CdO_2S_2$	$C_{48}H_{62}CdN_4O_2$	$C_{44}H_{42}CdO_4$	$C_{44}H_{42}CdO_2S_2$	$C_{36}H_{54}CdO_8$	$C_{74}H_{52}O_4S_4Cd_2$
formula weight	667.22	699.34	839.42	747.18	779.30	727.19	1356.82
cryst system	monoclinic	triclinic	monoclinic	triclinic	tetragonal	monoclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P4cc$	$P2_1/c$	$Pnna$
a, Å	9.4957(10)	9.251(2)	19.249(5)	8.868(2)	16.299(2)	9.343(4)	17.471(4)
b, Å	11.7841(13)	9.493(2)	15.152(2)	11.066(2)	16.299(2)	22.236(8)	27.146(5)
c, Å	15.858(2)	11.516(2)	18.085(3)	19.554(4)	15.497(3)	9.694(4)	15.246(3)
α, deg		74.74(3)		78.38(3)			
β, deg	93.659(12)	88.92(3)	117.46(2)	83.29(3)	90	117.86(3)	90
γ, deg		64.95(3)		73.51(3)			
V, $Å^3$	1770.9(3)	883.4(3)	4680(2)	1798.4(6)	4117.0(10)	1780.6(12)	7231(2)
Z	2	1	4	2	4	2	4
d (calcd), g/cm^3	1.251	1.315	1.191	1.380	1.257	1.356	1.246
absorp coeff, mm^{-1}	0.649	6.263	0.505	5.193	0.665	0.661	6.165
λ, Å	0.71073	1.54178	0.71073	1.54178	0.71073	0.71073	1.54178
no. of total reflns	3315	2825	8512	5642	1422	2027	3559
no. of unique reflns	3115	2639	8223	5322	1422	1918	3559
T, K	193	163(2)	293(2)	193(2)	193(2)	193(2)	163(2)
R,[a] %	6.41	6.95	7.44	5.86	8.61	6.67	12.24
R_w,[a] %	17.30	17.80	13.87	13.14	20.22	17.27	27.04

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

min; 0.352 g (98%) of the product was collected. Anal. Calcd for $C_{44}H_{42}O_2S_2Cd$: C, 67.81; H, 5.43. Found: C, 65.63; H, 5.85. ^1H NMR (C_6D_6): δ 1.47 [4H, m, {THT}], 2.55 [4H, m, {THT}], 6.8−7.4 [13H, m-br, {2,6-$Ph_2C_6H_3$-}]. $^{13}C\{H\}$ NMR (C_6D_6): δ 31.25 {THT}, 31.91 {THT}, 126−131 {2,6-$Ph_2C_6H_3$}, 168.1 {*ipso*-C_6H_3}.

Synthesis of Cd(O-2,6-${}^tBu_2C_6H_3$)$_2$(propylene carbonate)$_2$ (6). A 2-mL toluene solution of 0.19 g (0.92 mmol) of 2,6-di-*tert*-butylphenol was added to a 2 mL of toluene solution of $Cd[N(SiMe_3)_2]_2$ (0.20 g, 0.46 mmol). Slightly more than 2 equiv of (±)-propylene carbonate (0.1 mL, 1.16 mmol) was added to the solution, and the mixture was stirred for 2 h. After concentrating the solution to half-volume, it was placed at −20 °C for 2 days while colorless crystals of **7** formed. The crystals were isolated upon removing the supernatant solution and quickly washing the crystals 3 × 5 mL with hexanes while keeping the flask cold. After drying for 10 min under vacuum, 0.177 g (53%) of pale yellow crystals were obtained. Anal. Calcd for $C_{36}H_{54}O_8Cd$: C, 59.46; H, 7.48. Found: C, 57.75; H, 7.37. ^1H NMR (C_6D_6): δ 0.48 [3H, d, {PC}], 1.36−1.56 [18H, d-br, {2,6-${}^tBu$-C_6H_3−}], 2.80 [1H, t, {PC}], 3.23 [1H, t, {PC}], 3.57 [1H, m, {PC}], 6.8 [1H, br, {4-O-C_6H_3}], 7.2 [2H, br, {3,5-O-C_6H_3}]. $^{13}C\{H\}$ NMR (C_6D_6): δ 18.57 {PC}, 31.45 {−C*Me*$_3$}, 33.42 {−*C*Me$_3$}, 69.9 {PC}, 72.9 {PC}, 117 {4-C_6H_3}, 125 {3,5-C_6H_3}, 139 {2,6-C_6H_3}, 166 {*ipso*-C_6H_3}.

Synthesis of [Cd(O-2,4,6-$Me_3C_6H_2$)$_2$]$_n$ (7). $Cd[N(SiMe_3)_2]_2$ (0.52 g, 1.2 mmol) was stirred with 10 mL of THF. A solution of 2,4,6-trimethylphenol (0.317 g, 2.6 mmol) in 5 mL of THF was added to the cadmium amide solution, and white precipitate began forming immediately. The mixture was stirred for 1 h, after which time the white solid was collected on a glass frit and dried overnight under vacuum. The yield, 0.445 g, of white powder is quantitative. Anal. Calcd for $C_{18}H_{26}O_2Cd$: C, 55.89; H, 6.77. Found: C, 55.22; H, 6.02. ^1H NMR (C_5ND_5): δ 2.58 [3H, s, {4-C_6-*C*H_3}], 2.79 [6H, s, {2,6-C_6-(*C*H_3)$_2$}], 7.87 [2H, s, {3,5-C_6H_2}]. ^{13}C NMR (C_5ND_5): δ 18.8 {−CH_3}, 20.9 {−CH_3}, 121.6 {2,6-C_6H_2}, 125.6 {3,5-C_6H_2}, 129.2 {4-C_6H_2}, 162.9 {*ipso*-C_6H_2}.

Synthesis of [Cd(S_2CO-2,6-$Ph_2C_6H_3$)]$_2$(*m*-O-2,6-$Ph_2C_6H_3$)$_2$ (8) and $^{13}CS_2$-Labeled Complex. A 20-mL benzene solution of complex **4** was prepared as above using 0.25 g (0.58 mmol) of $Cd[N(SiMe_3)_2]_2$ and 0.228 g (1.16 mmol) of 2,6-diphenylphenol. Two equivalents of CS_2 (0.07 mL, 0.088 g) or 1 equiv of $^{13}CS_2$ was added by syringe. The solution was stirred overnight, then was filtered to remove any precipitate. The supernatant solution was placed under vacuum to remove the solvent and reaction byproducts, and a pale yellow crystalline solid was obtained in 58% yield (0.180 g.) Alternatively, crystals large enough to use for single-crystal X-ray diffraction formed within a few days from the concentrated benzene solution. Anal. Calcd for $C_{74}H_{52}O_4S_4Cd_2$: C, 65.44; H, 3.86. Found: C, 65.16; H, 4.11. IR (C_6H_6): $\nu(CS_2)$ 1152, 1058 cm^{-1}; $\nu(^{13}CS_2)$ 1129, 1023 cm^{-1}. ^{13}C NMR (C_6D_6): δ 231.4 (O^{13}*C*S_2).

^{113}Cd NMR Experiments. Samples of **1**−**6** were prepared in CD_2Cl_2, each approximately 0.05 M in Cd complex. Spectra were obtained at 20 °C intervals between 20 and −87 °C. After the sample had warmed to room temperature, an 8 mol excess of the respective coordinating donor solvent was added, and another set of spectra were collected. A 0.05 M sample of **7** was prepared in pyridine, and spectra were collected only at 20 and −30 °C. Small molecule insertion reactions were performed on similar samples in C_6D_6 or CD_2Cl_2 at room temperature.

X-ray Crystallographic Study of 1−6 and 8. Crystal data and details of the data collections are given in Table 1. Colorless block crystals of **1**−**6** and **8** were mounted of a glass fiber with epoxy cement at room temperature and cooled to 193 K (**1**, **3**, **5**, and **6**) or 163 K (**2**, **4**, and **8**) in a N_2 cold stream. Preliminary examination and data collection were performed on a Siemens P4 X-ray diffractometer for **1**, **3**, **5**, and **6** (Mo Kα $\lambda = 0.710\,73$ Å radiation) and a Rigaku AFC5 X-ray diffractometer for **2**, **4**, and **8** (Cu Kα $\lambda = 1.541\,78$ Å radiation.) Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections. ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \le 2\theta \le 50.0°$ for **1**, **3**, **5**, and **6** and for $8.0° \le 2\theta \le 120.0°$ for **2**, **4**, and **8**. Three control reflections collected for every 97 reflections showed no significant trends. Background measurements by stationary-crystal and stationary-counter techniques were taken at the beginning and end of each scan for half of the total scan time. Lorentz and polarization corrections were applied to the total reflections for each complex, listed in Table 1. A semiempirical absorption correction was applied to all complexes. Totals of unique reflections for each complex (Table 1) with $|I| \ge 2.0s_I$ were used in further calculations. Structures were solved by direct methods [SHELXS, SHELXTL-PLUS program package, Sheldrick (1993)]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded *R*, $R_w(F^2)$, and *S* values at convergence for all complexes, listed in Table 1. Hydrogen atoms were placed idealized positions with isotropic thermal parameters fixed at 0.08. Neutral-atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.[10]

Results and Discussion

The syntheses of complexes **1**−**5** are all carried out in a similiar manner. Specifically, 2 equiv of 2,6-disubstituted phenol is reacted with pure $Cd[N(SiMe_3)_2]_2$ in the appropriate

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(10) Ibers, J. A., Hamilton, W. C., Eds.; *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

donor solvent, as shown in eq 2 . Alternatively, complex **6** is

$$\mathrm{Cd[N(SiMe_3)_2]_2} + 2\ \mathrm{2,6\text{-}R_2C_6H_3OH} \xrightarrow{\text{donor solvent}}$$
$$\mathrm{R} = {}^{t}\mathrm{Bu}\ (\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{6})$$
$$\mathrm{Ph}\ (\mathbf{4}, \mathbf{5})$$
$$\mathrm{Cd(O\text{-}2,6\text{-}R_2C_6H_3)_2(donor)}_n + 2\ \mathrm{HN(SiMe_3)_2} \quad (2)$$
$$\text{donor} = \mathrm{THF}\ (\mathbf{1}, \mathbf{4})\ \mathrm{THT}\ (\mathbf{2}, \mathbf{5}),\ \mathrm{py}\ (\mathbf{3}),\ \mathrm{PC}\ (\mathbf{6})$$
$$n = 2 \text{ or } 3$$

formed by addition of slightly greater than 2 equiv of propylene carbonate (PC) to a reaction solution of the two reagents (eq 2) in toluene. The use of the bis(bis(trimethylsilylamide)) complex of Cd as the starting material is the only route we have found to cleanly form the bis(phenoxides), since metathesis reactions utilizing the Cd(II) halides results in mixed halide−phenoxide complexes. A color change from colorless to yellow or pale yellow occurs immediately upon mixing the reagents, as the exothermic reaction quickly takes place. The products are best isolated through crystallization from a concentrated reaction solution because precipitation or removal of all solvent under vacuum will result in loss of the donor ligands. Unfortunately, since the complexes are so soluble even at low temperature, the yields of products obtained in this fashion are variable and not always high, although it appears that this acid−base reaction does proceed to completion. The donor ligands are somewhat labile even in the solid state. Prolonged (longer than 20 min) periods in vacuo will remove or partially remove them in most cases, and decomposition will occur. Evidence of the loss of the coordinated donor groups can be found in ^{1}H NMR integrations and leads to inexact results in elemental analyses (Experimental Section).

The same methodology (eq 2) was employed for the preparation of a complex which had a less sterically bulky phenol, 2,4,6-trimethylphenol, using THF as solvent. The product, $[\mathrm{Cd(O\text{-}Me_3C_6H_2)_2}]_n$ (**7**), is observed to precipitate immediately upon mixing the reagents, regardless of the amount of solvent used. Presumably an aggregate species with bridging phenoxides,[11] **7**, is soluble only in pyridine and can be dissolved by addition of approximately 4 mol of pyridine to the THF reaction mixture. Crystals of **7** suitable for X-ray diffraction have not been obtained thus far. It is expected that the complex crystallized from a pyridine solution would adopt a tetrahedral geometry with two coordinated pyridine molecules, similar to that which has been defined for its Zn analogue, $\mathrm{Zn(O\text{-}2,4,6\text{-}Me_3C_6H_4)_2(py)_2}$.[3] The smaller methyl groups on the phenoxide rings should not impose linearity of these ligands; however, more than two pyridines may be able to coordinate to the cadmium center, as is found in complex **3**.

All complexes **1**−**6** have been characterized by X-ray crystallography, and a list of selected bond lengths and angles is provided in Table 2. Complexes **1** and **2** which contain the same *tert*-butyl-substituted phenol but the different donor ligands THF and THT, respectively, both adopt a crystallographically imposed square-planar geometry about the metal center which is very rare for Cd(II) complexes. A thermal ellipsoid representation of **1** is shown in Figure 1. The Cd−O(phenoxide) bond length in **1** of 2.058 Å is slightly shorter than that found in **2,** 2.102(6) Å. On the other hand, the Cd−O(THF) bond length for the ether ligands at 2.465(3) Å is comparable to that observed for the Cd−S(THT) bond if the difference in covalent radii of oxygen and sulfur (0.3 Å) is taken into account. Apparently, neither THF nor THT is a strong enough donor ligand to cause any distortion in the linear O(phenol)−Cd−O(phenol) fragment. However, when pyridine is used as the

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **1**−**6**[a,b]

Complex **1**: $\mathrm{Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(THF)_2}$			
Cd(1)−O(1)	2.068(3)	Cd(1)−O(2)	2.465(3)
O(1)−C(1)	1.341(5)		
O(1)−Cd(1)−O(1A)	180.0	C(1)−O(1)−Cd(1)	126.0(2)
O(1)−Cd(1)−O(2)	81.53(11)	Cd(1)−O(2)−($\mathrm{C_4H_8}$ plane)	174.1
O(1)−Cd(1)−O(2A)	89.47(11)		
Complex **2**: $\mathrm{Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(THT)_2}$			
Cd(1)−O(1)	2.102(6)	Cd(1)−S(1)	2.768(2)
O(1)−C(6)	1.343(10)		
O(1)−Cd(1)−O(1A)	180.0	O(1)−Cd(1)−S(1)	77.7(2)
O(1)−Cd(1)−S(1A)	102.3(2)	C(6)−O(1)−Cd(1)	125.3(5)
		Cd(1)−S(1)−($\mathrm{C_4H_8}$ plane)	125.6
Complex **3**: $\mathrm{Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(py)_3}$			
Cd(1)−O(1)	2.193(5)	Cd(1)−O(2)	2.190(5)
Cd(1)−N(1)	2.342(7)	Cd(1)−N(2)	2.347(6)
Cd(1)−N(3)	2.372(6)	O(1)−C(1)	1.314(9)
O(1)−Cd(1)−O(2)	156.1(2)	O(1)−Cd(1)−N(1)	102.4(2)
O(1)−Cd(1)−N(2)	92.5(2)	O(1)−Cd(1)−N(3)	88.4(2)
Cd(1)−O(1)−C(1)	165.0(5)	N(3)−Cd(1)−N(2)	169.7(2)
Complex **4**: $\mathrm{Cd(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THF)_2}$			
Cd(1)−O(1)	2.073(5)	Cd(1)−O(2)	2.074(5)
Cd(1)−O(3)	2.320(6)	Cd(1)−O(4)	2.293(6)
O(1)−C(1)	1.307(9)		
O(1)−Cd(1)−O(2)	150.1(2)	O(3)−Cd(1)−O(4)	83.1(3)
O(1)−Cd(1)−O(3)	92.4(2)	O(1)−Cd(1)−O(4)	107.5(2)
C(1)−O(1)−Cd(1)	130.1(5)	C(19)−O(2)−Cd(1)	120.0(4)
Cd(1)−O(3)−($\mathrm{C_4H_8}$ plane)	172.7	Cd(1)−O(4)−($\mathrm{C_4H_8}$ plane)	169.4
Complex **5**: $\mathrm{Cd(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THT)_2}$			
Cd(1)−O(1)	2.12(2)	Cd(1)−S(1)	2.634(9)
C(1)−O(1)	1.34(3)		
O(1)−Cd(1)−O(1A)	93.8(11)	S(1)−Cd(1)−S(1A)	84.3(4)
O(1)−Cd(1)−S(1)	157.5(5)	O(1)−Cd(1)−S(1A)	95.1(6)
C(1)−O(1)−Cd(1)	133(2)	Cd(1)−S(1)−($\mathrm{C_4H_8}$ plane)	114
Complex **6**: $\mathrm{Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(PC)_2}$			
Cd(1)−O(1)	2.038(8)	Cd(1)−O(2)	2.393(8)
C(1)−O(1)	1.359(12)	O(2)−C(15)	1.177(19)
O(1)−Cd(1)−O(1A)	180.0	O(2)−Cd(1)−O(2A)	180.0
O(1)−Cd(1)−O(2)	83.7(3)	O(1)−Cd(1)−O(2A)	96.3(3)
Cd(1)−O(1)−C(1)	128.3(6)	Cd(1)−O(2)−C(15)	128.4(11)

[a] Estimated standard deviations given in parentheses. [b] Symmetry-generated atoms designated by (*X*A).

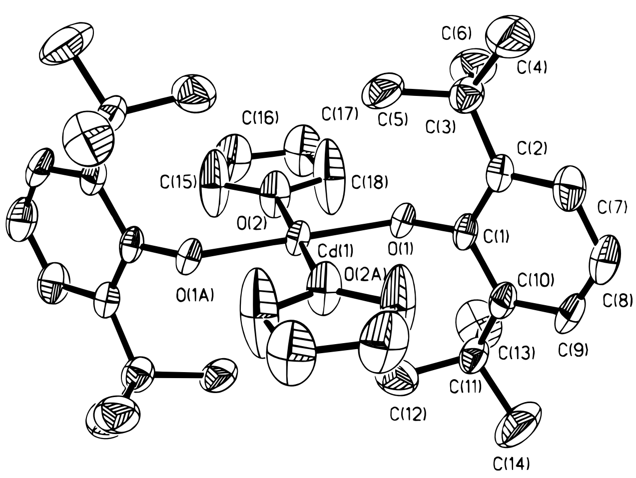

Figure 1. Thermal ellipsoid representations of $\mathrm{Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(THF)_2}$ (**1**) (50% probability).

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(11) (a) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269. (b) Melhotra, K. C.; Martin, R. L. *J. Organomet. Chem.* **1986**, *239*, 159.

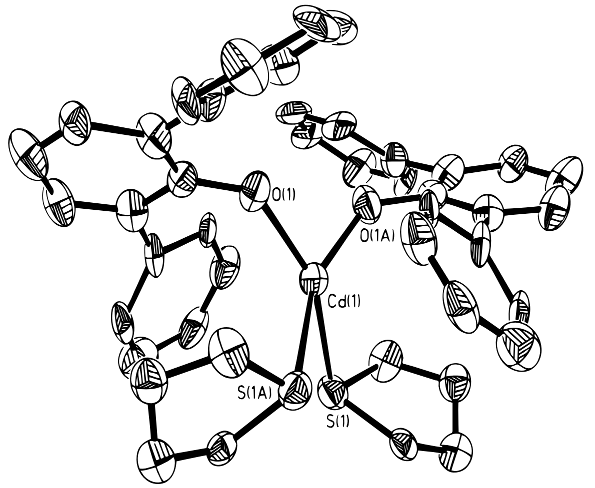

Figure 2. Thermal ellipsoid representation of Cd(O-2,6-Ph$_2$C$_6$H$_3$)$_2$(THT)$_2$ (**5**) (50% probability).

donor with the same phenoxy ligands, distortion from square planar geometry is attained by the coordination of a third pyridine molecule. Complex **3**, Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(py)$_3$, displays a solid-state trigonal bipyramidal structure with two axial pyridines and phenoxides in equatorial positions.[8] The average Cd−O(phenoxide) bond distance is 2.192(5) Å, and the angle, O(1)−Cd-O(2), between the phenoxide ligands is 156.1(2)°. Solution studies addressed in the next section suggest that complex **3** forms in a stepwise process, initially affording either a square-planar or distorted tetrahedral bis(pyridine) derivative, which can subsequently bind another pyridine base at low temperatures in solution or in the solid state.

As anticipated, distortion from the unique square-planar geometry is also obtained when the ortho groups on the phenoxy ligands are sterically smaller and less basic than the bulky electron-donating *tert*-butyl. The 2,6-diphenylphenoxide derivative of complex **1** has been found to have the distorted tetrahedral geometry expected for a four-coordinate d^{10} metal complex, similar to its zinc analogue.[3] Cd(O-2,6-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$ (**4**) and its THT derivative (**5**) shown in Figure 2 have been found to have similar Cd−phenoxy and Cd−donor bond lengths but largely different bond angles around the metal center. The Cd−O(phenoxide) bond length of 2.12(2) Å in **5** is approximately 0.05 Å longer than those in **4**, but the angle between these two phenoxide ligands is drastically smaller in **5** at 93.8(11)° than that in **4** of 150.1(2)°. The Cd−S(THT) bond length, 2.634(9) Å, is comparable to the Cd−O(THF) bond distance, again once the difference in ionic radii is taken into account, and the angle between the two donor ligands, 84.3(4)°, is also very similar. The difference between the orientations of the phenoxide ligands with respect to the cadmium center in **4** and **5** probably results from steric congestion about the cadmium center in the latter derivative. That is, the sulfur donor ligands in complex **5** are pyramidal (angle defined by the Cd−S vector and the midpoint of the SC$_2$ plane is 114.1°), thereby causing steric interactions between the phenoxide ligands and the heterocyclic ring systems. This steric repulsion leads to a closing of the O(1)−Cd−O(1A) angle. On the other hand, the THF donor ligands are more accommodating of the bulky phenoxide groups in this d^{10} metal complex and adopt a more linear arrangement: Cd−O(1)−[OC$_2$ plane] and Cd−O(2)−[OC$_2$ plane] are 164.4 and 172.7°, respectively. Similar ether and thioether binding parameters are seen in the square-planar derivatives, **1** and **2**, where the corresponding angles are 174.1 and 125.6°.

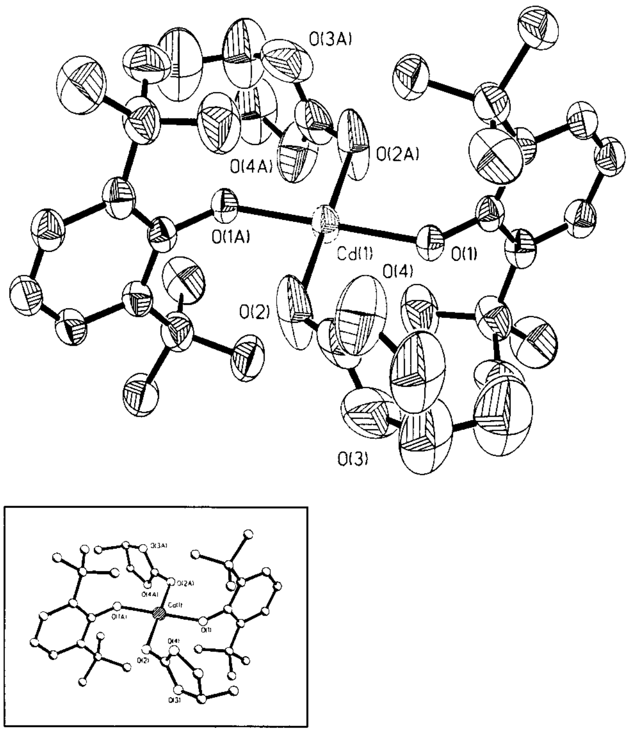

Figure 3. Thermal ellipsoid representation of Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(PC)$_2$ (**6**) (50% probability) with inset of ball-and-stick drawing.

Finally, as we were exploring the effect of donor ligands on coordination number and geometry, we recalled that cyclic carbonates are also excellent donor solvents. Complexes of our catalysts with this ligand and the study of its coordination ability would be particularly interesting since cyclic carbonates are the byproduct, or in some cases the only product, of CO$_2$ and epoxide coupling with the Zn and Cd catalysts. Strong coordination could mean that these donors have the potential to act as inhibitors in the polymerization system. Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(propylene carbonate)$_2$ was synthesized in toluene solution with addition of a slight excess of 2 equiv of the high-boiling donor base. The structure of this complex, as shown in Figure 3, again has a crystallographically imposed square-planar geometry about the metal center. The Cd−O(phenoxide) bond distance of 2.038(8) Å is slightly shorter than that same bond in **1**; however, the Cd−O(PC) distance of 2.393(8) Å is over 0.1 Å shorter than the Cd−O(THF) distance in **1**. All bond angles in **6** are comparable with those in the other square-planar complexes. The Zn analogue to this complex has recently been prepared and characterized in our laboratories, and it adopts distorted-tetrahedral geometry and has a Zn−O(PC) bond distance of 2.071(11) Å.[3] The carbonyl bond length of the coordinated propylene carbonate in **6**, 1.177(19) Å, may be compared with that in the Zn analogue, 1.20(2) Å, and with that reported for free ethylene carbonate, 1.15 Å,[12] to assess the degree of weakening of the double bond upon coordination.

Solution Studies. In Caulton's previous report on the soluble zinc(II) phenoxide complexes, it was noted that the THF ligands, while coordinated in the solid-state, are labile in solution. On the basis of ^{1}H NMR evidence of Zn(O-2,4,6-^{t}Bu$_3$C$_6$H$_2$)$_2$(THF)$_2$ in benzene solutions, it was believed that only one of the THF ligands was dissociating, leaving a three-coordinate, soluble Zn bis(alkoxide) species that could act as a catalyst.[2,13] The experiments discussed here were done to examine the coordina-

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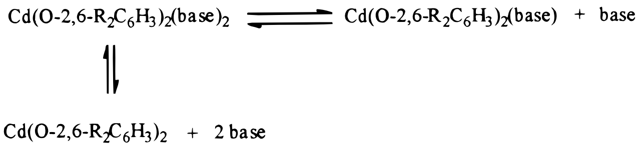
(12) Brown, C. J. *Acta Crystallogr.* **1954**, *7*, 92.

Table 3. ^{1}H Chemical Shifts of Donor Solvents in C_6D_6 Solutions at 20 °C^{a,b}

complex (donor solvent)	chemical shifts (β, α, ppm)	difference from free (ppm)
1 (THF)	1.25, 3.48	0.18, 0.07
2 (THT)	1.38, 2.47	0.14, 0.10
3 (py)	6.58, 6.9, 8.53	0.15, 0.15, 0.01
4 (THF)	1.43, 3.58	0, 0.03
5 (THT)	1.47, 2.55	0.05, 0.02
6 (PC)	0.48, 2.80, 3.23, 3.57	0.23, 0.33, 0.38, 0.36
$Zn(2,6\text{-}^tBu_2C_6H_3)_2(THF)_2$	1.13, 3.40	0.30, 0.15
$Zn(2,6\text{-}Ph_2C_6H_3)_2(THF)_2$	1.19, 3.11	0.24, 0.44

[a] The chemical shift difference from free solvent in benzene is also given. [b] Free solvents in benzene solution: THF, δ 1.43, 3.55; THT, δ 1.52, 2.57; py, δ 6.73, 7.05, 8.54; PC δ 0.71, 3.13, 3.61, 3.93.

Scheme 2



tion of the cadmium analogues to the donor bases in solution with the aid of ^{113}Cd NMR.

All complexes **1**−**7** were first studied by ^{1}H NMR in benzene or methylene chloride solutions. Even at room temperature, the spectra exhibit chemical shifts for the donor base ligands which are located upfield from that expected for the free solvent in solution. Table 3 lists the chemical shifts for the base ligands of these complexes in benzene-d_6 solutions and the difference (parts per million) from the free solvent in benzene.

There are a few trends from Table 3 to which attention should be given. First, the chemical shift difference of the protons β to the heteroatom is in almost all cases greater than that for the α-protons. It would be expected that, as coordination to a metal occurs, the atoms closest to the donor atom would experience the greater change in electronic environment. Second, the shift differences for Zn complexes are larger than those for the Cd analogues, which would be anticipated as Zn is a better Lewis acid. Third, there is practically no chemical shift difference for complexes **4** and **5**, both of which contain the 2,6-diphenylphenoxide ligands, while those complexes which have *tert*-butyl- substituted phenoxides (**1**, **2**, **3**, and **6**) seem to be interacting with the donor solvents.

It is not possible to ascertain from the ambient temperature spectra if these peak positions of the bases are representative of clearly coordinate or uncoordinated donor molecules or rapid exchange between free and coordinated solvent. An equilibrium between free and bound solvent could be imagined to exist in one of two ways, as illustrated in Scheme 2.

To investigate the possibilities, ^{1}H NMR spectra of some of these complexes at variable temperatures were obtained in benzene (higher temperature) or methylene chloride (lower temperature) solutions. When a CD_2Cl_2 solution of **2** was cooled to −87 °C, all peaks, phenoxide and base, show an additional upfield shift of only 0.1 ppm and the peaks broaden slightly. Alternatively, the low-temperature spectra of complex **3** is more interesting because, once below −80 °C, the peak representative of the *tert*-butyl groups and the pyridine signals each split into two broad peaks. This could be due to the coordination of a third pyridine as the equilibrium is slowed, which distorts an otherwise symmetric square-planar complex. The *tert*-butyl signal is similarly split in the room-temperature spectrum of **6**, which must be a consequence of coordination (or equilibrium shifted largely toward coordination) of the unsymmetric PC ligands, whereas warming the sample leads to a single peak, presumably as PC dissociates. This splitting is more pronounced in CD_2Cl_2 solution as the solvent induces larger chemical shift differences between the two peaks. Coordination of THF in **1**, THT in **2**, or two pyridine molecules in **3**, which is suggested by the large shifts from free solvent, would not be expected to cause this splitting due to the symmetry of the ligands and the final complex.

Table 4. ^{113}Cd NMR Chemical Shifts Obtained in CD_2Cl_2 Solutions (referenced to 0.1 M $Cd(ClO_4)_2$ in D_2O)

complex	core atoms in structure	δ (ppm) at 20 °C	*d* (ppm) −80 °C
1	O_4	−2	21
2	O_2S_2	144	221
3	O_2N_3	109	50
4	O_4	73	53
5	O_2S_2	76	254
6	O_4	5	−17
7	O_2N_x	113^a	

[a] Complex **7** was run in a C_6D_5N solution.

The data from the ^{113}Cd NMR have given a better picture of the cadmium coordination sphere. Table 4 lists the chemical shifts of Cd complexes in CD_2Cl_2 solutions. These are the first reported for Cd phenoxides or alkoxides in solution.[8] The only other example of a four-coordinate Cd complex with only O donors for which a solution ^{113}Cd NMR shift is reported is the tetrahedral phosphine oxide complex, $[Cd(OP(C_6H_{11})_3)_4][AsF_6]_2$, which displayed a single peak at 94 ppm in SO_2 solution.[14] Data in the literature for Cd−O complexes have been mainly from studies of either oxyanion salts of Cd^{2+} in aqueous solutions or the metal complexed by large chelating agents. In most of these studies, the Cd complexes are presumed to be of octahedral or higher coordination.[15]

The room-temperature peak positions suggest that complexes **4** and **5** have the same structure in solution, and thus, that there is no interaction with their donor ligands. The complexes **3** and **7** are also believed to have a similar coordination sphere at ambient temperature, based on the peak positions, most probably that of a bis(phenoxide) with two coordinated pyridine ligands. That the peak positions for complexes **1**, **2**, **3,** and **6** are quite different despite having the same phenoxide ligands is evidence consistent with the ^{1}H NMR data for the interaction of THF, THT, pyridine, and PC, respectively, with the metal center. It is interesting to note the difference in the low-temperature peak positions for complexes which contain the same core atoms but vary in the substituents on the phenoxides. Whether this stems from the basicity of the phenoxide or the geometry of the complex, or a combination of both, is not discernible from these data alone.

It is most likely that the coordination of the donor solvents occurs as an equilibrium process. The spectra obtained at intervals between 20 and −80 °C for **2** and **5**, illustrated in Figure 4, are representative of the two types of substituted phenoxide complexes. In the series of spectra for **5**, a second

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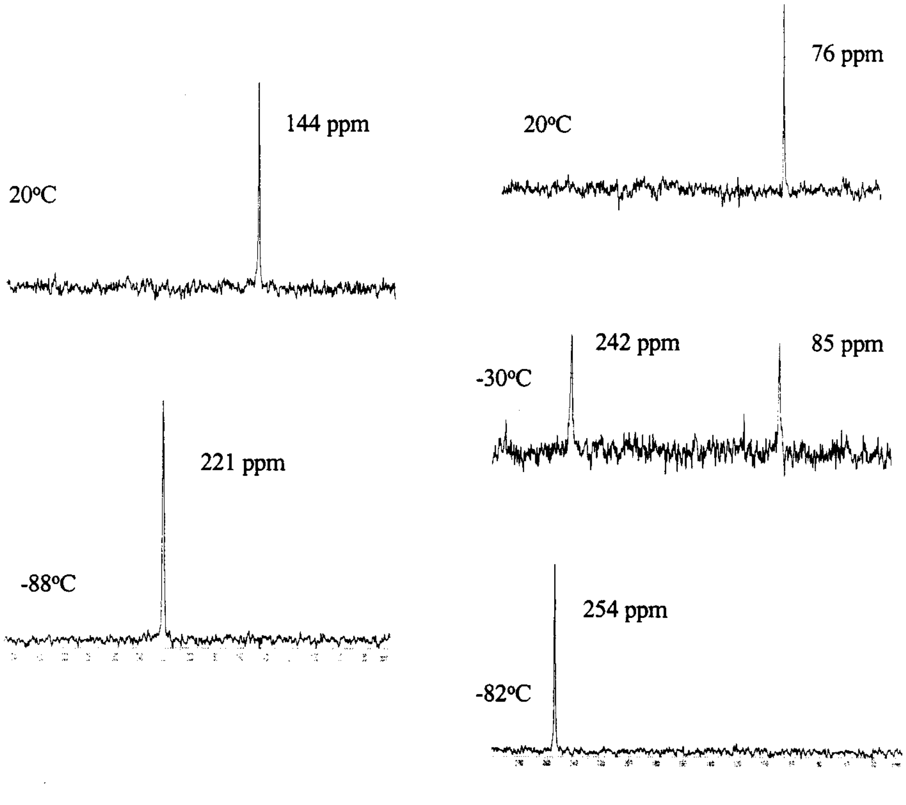
(13) Temperature-dependent ^{1}H NMR studies from our laboratories on the $Zn(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THF)_2$ complex in CD_2Cl_2 have clearly demonstrated that the THF ligands are dissociated at ambient temperature, with exchange between free and bound THF being slowed below −85 °C.

(14) Dean, P. A. W. *Can. J. Chem.* **1981**, *59*, 3221.

(15) (a) Armitage, I. M.; Pajer, R. T.; Schoot Uiterkamp, A. J. M.; Chlebowski, J. F.; Coleman, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 5710. (b) Summers, M. F. *Coord. Chem. Rev.* **1988**, *86*, 43 and references therein. (c) Ellis, P. D. In *The Multinuclear Approach to NMR Spectroscopy*; NATO ASI Series C103; Lambert, J. B., Riddell, F. G., Eds.; D. Reidel Pub.: Boston, MA, 1983; p 457 and references therein.



(a) (b)

Figure 4. ^{113}Cd NMR spectra for complexes **2** and **5** at variable temperatures. Spectra for (a) complex **2** and (b) complex **5**.

peak is seen to emerge as the temperature is lowered while the intensity of the original peak decreases. This does imply that the conversion from the 2-coordinate complex to the 4-coordinate complex proceeds with no intermediate. Because two signals can be seen in the spectra for **4** and **5**, it follows that the rate of exchange between coordinated and noncoordinated solvent must be slower than 1.6×10^4 s^{-1} for **5** and 1.8×10^3 s^{-1} for **4**. The observation of only one signal for **2** and its analogues, along with the position of the peak, implies that the equilibrium is shifted well toward the 4-coordinate complex even at room temperature and that the exchange rate is very fast, leading to only a single averaged signal.

Insertion Reactions. Insertion of CO_2, COS, and CS_2 into M$-$O bonds is well-known to occur rapidly,[16] so insertions of the these small molecules into Cd$-$phenoxide bonds have been examined by ^{13}C and ^{113}Cd NMR. This is of interest also to determine if CO_2 insertion occurs prior to epoxide ring opening in the mechanistic pathway for the copolymerization. When ^{13}C-labeled CO_2 was bubbled into an NMR samples of dichloromethane-d_2 solutions of **4**, no reaction was observed visibly or through its ^{13}C NMR spectrum. The spectrum showed only the intense signal at 125 ppm for free $^{13}CO_2$, even after 15 h, by which time, insoluble white precipitate had begun to form in the NMR tube. It was presumed that CO_2 insertion did not occur immediately because of the steric hindrance of the phenyl groups ortho to the Cd$-$phenoxide bond[16] but that, over time, insertion may have taken place through some type of deconstructive pathway, leading to insoluble polymeric carbonate compounds and phenol. The insertion of COS into complex **4** was then tried, as the formation of a strong Cd$-$S bond derived from a weaker C$=$S bond might facilitate the reaction to give a thiocarbonate complex. The reaction was followed by ^{113}Cd NMR. Within minutes of bubbling COS through the sample, a ^{113}Cd resonance was observed at 131 ppm, downfield from that of **4** at 76 ppm, corresponding to the formation of a Cd$-$S bond. For comparison, an identical reaction was tried with 2 equiv of CS_2 added to a sample of **4**. The new ^{113}Cd NMR signal was at 146 ppm for the CS_2-insertion product. Possibly, interaction of the Cd center with the distal S atom could produce a more deshielded chemical shift relative to that of the COS product; however, the two products should have comparable structures.

The product of CS_2 insertion into complex **4** was isolated and characterized crystallographically. Although the data were of poor quality and the structure was highly disordered, we can determine that insertion occurs only at one M$-$O bond, as shown in the drawing in Figure 5. The crystals of $[Cd(S_2CO\text{-}2,6\text{-}Ph_2C_6H_3)]_2[\mu\text{-}(O\text{-}2,6\text{-}Ph_2C_6H_3)_2]$ (**8**) were grown from benzene solution; thus, with no donor ligands present, dimer formation is observed. Infrared and ^{13}C NMR spectroscopies data were also collected to verify that the insertion reaction yields this complex in solution. The CS_2 stretches in the IR spectrum were difficult to discern, so the complex was synthesized again using $^{13}CS_2$. The IR peaks at 1152 and 1058 cm^{-1} ($\Delta\nu$ = 94 cm^{-1}) in the spectrum of the nonlabeled complex were observed to shift to 1129 and 1023 cm^{-1} in the spectrum of the ^{13}C-labeled complex (see Figure 6.) The small difference between the asymmetric and symmetric $\nu(CS_2)$ stretching frequencies is indicative of a chelating coordination[17] of the dithiocarbonate unit which is found in the solid-state structure.

The ^{13}C-labeled complex was also used to obtain the ^{13}C NMR peak position for **8** at 231 ppm for the dithiocarbonate's

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[16] Darensbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Chojnacki, S. S.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 2418.

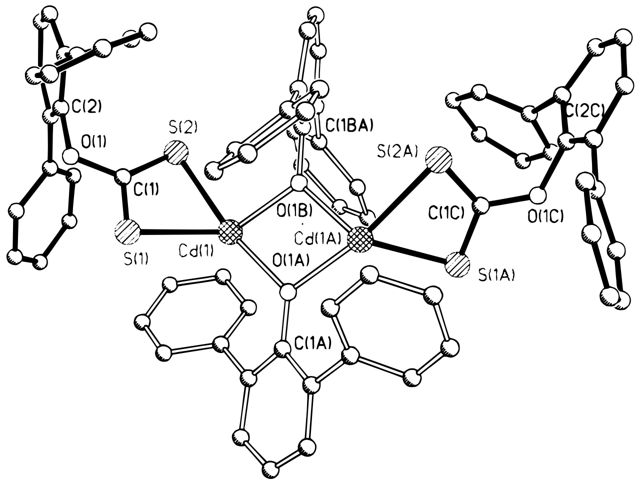

Figure 5. Ball-and-stick drawing of complex **8**.

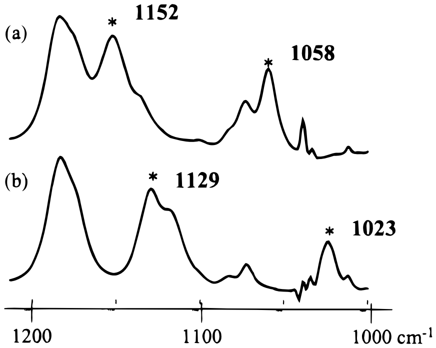

Figure 6. Infrared spectra for (a) CS_2 insertion and (b) $^{13}CS_2$ insertion into complex **4** in benzene solution.

carbon atom. Very little ^{13}C NMR data are available for comparison for complexes of CS_2 which might allow inferences to structure based on peak position. Products of simple CS_2 insertion into zero-valent metal−aryl oxide bonds have been reported to display peaks in their ^{13}C NMR spectra around 200 ppm;[18] however, a more recent report of dithiocarbonate complexes of tellurium(IV) has listed peak positions further downfield for several complexes with anisobidentate dithiocarbonate ligands. Furthermore, the $-S_2COR$ peak for the potassium salts of the ligands was seen at 233 pm and considered to be representative of complexes which have bidentate ligands.[19]

An NMR-scale reaction of complex **2** in benzene with $^{13}CO_2$ and with $^{13}CS_2$ was also completed using ^{13}C NMR to monitor the reactions. Again, no insertion was observed for $^{13}CO_2$. The reaction did occur for $^{13}CS_2$, with the product peak occurring at 234 ppm, comparable to that observed for insertion into **4**. The reaction of COS with **2** was followed by ^{113}Cd NMR since the ^{13}C-labeled reagent is not readily available. A sample of complex **9** in C_6D_6 displays a room-temperature signal at 148 ppm. The spectrum obtained within minutes of bubbling COS through this sample displayed a peak at 431 ppm which would be consistent with at least one M−O insertion with ligation through the S, causing the large downfield shift. This chemical shift is much farther downfield than that observed for the reaction of COS with **2**, and the structure of this complex may be beyond a simple insertion product, perhaps including bridging thiocarbonate ligands. Additional studies are needed to better characterize the nature of this species.

Catalytic Activity. The cadmium complex **7** was examined for its activity as a catalyst for the copolymerization of cyclohexene oxide with CO_2. This complex was chosen because its Zn analogue has been found to be the most active of our Zn bis(phenoxide) catalysts.[3] The golden-colored solution obtained after the high-pressure reaction was analyzed by IR spectroscopy. The spectrum contained a peak in the carbonate stretching region at 1750 cm^{-1} indicative of polycarbonate linkages. Removal of the epoxide solvent yielded a sticky, transparent polymer which is soluble in methanol, an indication that the product is of low molecular weight. The starting material $Cd[N(SiMe_3)_2]_2$ was also tried as a catalyst because it had been found to rapidly homopolymerize cyclohexene oxide. The product solution obtained after a run identical to the previous one again exhibits an IR peak at 1750 cm^{-1} and the isolated product is a sticky, methanol-soluble polymer film. Nevertheless, the Cd complex clearly catalyzed formation of polymer product, however, with a greatly reduced activity relative to its zinc analogue. However, the concentration of Cd used in these catalytic runs was three times the usual amount of Zn used. When a run was executed using **7** at a Cd concentration (0.034 g with 10 mL of epoxide) which was the same as the usual Zn concentration, very little polymer was formed. It is of importance to note here that, although the cadmium complexes containing the bulky phenoxide ligands (e.g., complex **4**) do not undergo insertion reactions with CO_2, these derivatives slowly catalyze the homopolymerization of epoxides. This observation is a consequence of the fact that CO_2 insertion *requires* interaction with the sterically blocked lone pairs on the phenoxide ligand, whereas the epoxide ring-opening process involves interaction of the epoxide at the metal center, much like the COS and CS_2 insertion processes.

Conclusions

Monomeric Cd aryloxides, $Cd(O\text{-}2,6\text{-}R_2C_6H_3)_2(donor)_2$, are easily synthesized by utilizing phenoxides which contain sterically bulky groups in the ortho ring positions, a tactic which has been found to work for many metals with aryl−chalcogenolate ligands. The family of complexes discussed within start with the same basic reaction but lead to a variety of Cd complexes with coordination modes reflecting the much richer coordination chemistry of cadmium as compared with zinc. With the characterization of several square-planar complexes, we have shown that while Buhro's complex is unusual it is not unique. As Buhro had suggested, the structure of these complexes appears to be controlled by the coordination of the sterically bulky phenoxide ligands.[7] When the smaller, less-basic 2,6-diphenylphenoxide is employed, distorted coordination is obtained with donors of varying strength, THF and THT, but the very bulky *tert*-butyl-substituted phenoxide complexes are not altered in structure for the different base ligands. Coordination of two donor molecules should be able to induce at least a small amount of distortion to the linear segment to give distorted-tetrahedral complexes,[20] as is observed for zinc with the same phenoxide ligands. However, it appears that the only way distortion will occur with the 2,6-di-*tert*-butyl phenoxy ligands is if the donor is strong enough, like pyridine, to coordinate additional molecules and, thus, override the tendency of the bulky phenoxides to be linear.

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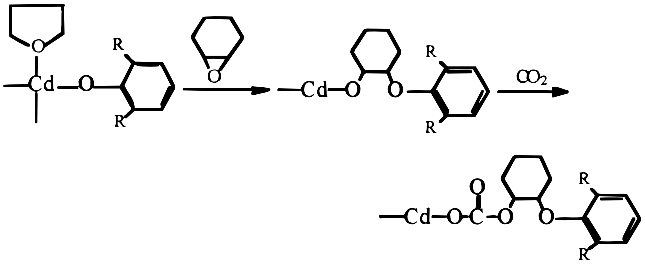
The solution studies of these complexes indicate that there is a difference in the ability of these complexes to coordinate bases depending on the basicity of the phenoxy ligands, with the less basic, phenyl-substituted phenoxides surprisingly showing little or no interaction at room temperature. The ^{113}Cd NMR results for these complexes are the first reported for monomeric phenoxides or alkoxides. The only trend which can be noted is the deshielding observed for complexes with the phenyl-substituted phenoxide as compared to their *tert*-butyl-substituted counterparts. This could be due to either the change in geometry of the complexes from tetrahedral to square planar or could be caused by ring-current effects.

The insertion reactions of CS_2 and COS and the lack of reactivity of CO_2 with these complexes have been very enlightening. While the steric bulk of the subtituents of the phenoxide ligands aids in formation of soluble monomers, it apparently will not allow insertion of CO_2.[21] This means that ring opening and insertion of *at least* one epoxide into the metal−phenoxide bond would have to occur first to remove the steric bulk from around the metal center, after which CO_2 insertion should easily occur as depicted in Scheme 3. These findings are totally consistent with earlier studies of tungsten model complexes involving CO_2, COS, and CS_2 insertion reactions into W−O bonds containing sterically bulky phenoxides.[16]

Scheme 3



Finally, it is notable that these cadmium phenoxides are catalytically active toward the copolymerization of CO_2 with cyclohexene oxide to give low-molecular-weight polymers. Cadmium is expected to have decreased activity as compared with zinc; however, it is much easier to propose comparisons between the Cd models and the Zn catalysts when they show some similarities in their catalytic function.

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Supporting Information Available: Ball-and-stick drawings and tables of anisotropic thermal parameters, bond lengths, and bond angles for complexes **1**, **5**, **6**, and **8** (26 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[21] Nevertheless, complex **7**, which contains sterically less encumbered phenoxide ligands, most likely readily inserts CO_2 as has been demonstrated for its zinc analogue dissolved in pyridine.[3.]