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Syntheses, Structures, and Binding Constants of Cyclic Ether and Thioether Adducts of Soluble Cadmium(II) Carboxylates. Intermediates in the Homopolymerization of Oxiranes and Thiiranes and in Carbon Dioxide Coupling Processes

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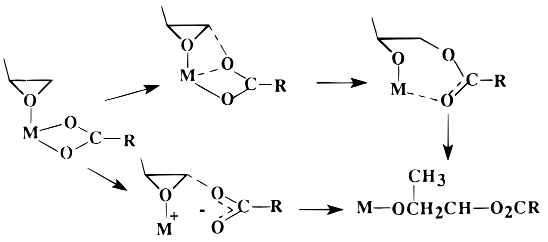
A synthetic methodology for the preparation of a large variety of η^3-HB(3-Phpz)$_3$Cd(acetate) adducts is presented which involves replacement of toluene in the η^3-HB(3-Phpz)$_3$Cd(acetate) solvate complex by the appropriate cyclic ether or cyclic thioether. In this manner, adducts of THF, dioxane, propylene oxide, cyclohexene oxide, and propylene sulfide were isolated. The solid-state structures of several of these complexes were determined by X-ray crystallography, revealing a six-coordinate complex where the acetate ligand is shown to be fairly symmetrically bonded to the cadmium center. In methylene chloride solution, the cyclic ether or thioether readily dissociates to afford the five-coordinate complex, as demonstrated by ^{113}Cd NMR. A quantitative assessment of the binding of these base adducts of η^3-HB(3-Phpz)$_3$Cd(acetate) was determined by measuring the temperature dependence of the equilibrium constants for the five- and six-coordinate derivatives. The presence of one sharp ^{113}Cd resonance in this equilibrium mixture is indicative of rapid intermolecular exchange between the five- and six-coordinate complexes when compared to the chemical shift differences in these two species (~6600 Hz at 89 MHz). The order established for ether binding is THF > dioxane > propylene sulfide > cyclohexene oxide ≥ propylene oxide, with $\Delta H°$ and $\Delta S°$ spanning the ranges −27.7 to 24.3 kJ/mol and −89.7 to −94.1 J/(mol K). The epoxide and thioepoxide adducts were shown to serve as models for the initiation step in the copolymerization of epoxides with carbon dioxide catalyzed by metal carboxylates. That is, the carboxylate ligand was shown to ring-open the epoxide or thioepoxide, subsequently affording polyethers or polythioethers with ester end groups. By way of contrast, in the presence of CO$_2$ and epoxides, this system led to cyclic carbonate production.

Introduction

We have been interested for some time in the copolymerization of epoxides with CO$_2$, which affords high-molecular-weight polycarbonates, a process first discovered by Inoue.[1] Dicarboxylates of Zn(II) were reported by Soga[2] to be the most active catalysts for this process and are being examined for use in commercial applications.[3] Nevertheless, these Zn(II) dicarboxylates are not very active and because they are extremely insoluble and noncrystalline, the exact structure of the active catalyst or catalyst precursor has not yet been determined. It has been proposed that the dicarboxylate chelates to the zinc center;[2] however it is likely that it has a layered structure with bridging dicarboxylates between the layers.[4] Additionally, definitive mechanistic aspects of this catalytic system are unavailable, due largely to the heterogeneous nature of the catalyst and also because of the limited spectroscopic probes available to Zn(II) systems. In part, our recent efforts have been directed toward designing soluble monomeric zinc catalysts which possess high catalytic activity and are amenable to mechanistic investigation.[5]

Scheme 1



The initiation of this copolymerization catalyzed by metal carboxylates could be considered to occur by either one of two possible routes after coordination of the epoxide to the metal, shown in Scheme 1. Although it is illustrated in Scheme 1 that alkyl cleavage occurs at the less hindered, more electropositive carbon center, this is not exclusively the case for the ring-opening process during the copolymerization reaction.[6]

Previously, we communicated the synthesis and X-ray crystal structures of two Cd(II) carboxylates, solubilized through the

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(1) (a) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B* **1969**, *7*, 287. (b) Inoue, S.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1969**, *130*, 210. (c) Inoue, S.; Koinuma, H.; Yokoo, Y.; Tsuruta, T. *Makromol. Chem.* **1971**, *143*, 97. (d) Kobayashi, M.; Inoue, S.; Tsuruta, T. *Macromolecules* **1971**, *4*, 658. (e) Kobayashi, M.; Tang, Y. L.; Tsuruta, T.; Inoue, S. *Makromol. Chem.* **1973**, *169*, 69. (f) Kobayashi, M.; Inoue, S.; Tsuruta, T. *J. Polym. Sci., Polym. Chem. Educ.* **1973**, *11*, 2383. (g) Kuran, W.; Pasynkiewicz, S.; Skupinska, J.; Rokicki, A. *Makromol. Chem.* **1976**, *177*, 11. (h) Kuran, W.; Pasynkiewicz, S.; Skupinksa, J. *Makromol. Chem.* **1976**, *177*, 1283. (i) Soga, K.; Uenishi, K.; Hosoda, H.; Ikeda, S. *Makromol. Chem.* **1977**, *178*, 893. (j) Soga, K.; Hyakkoku, K.; Ikeda, S. *Makromol. Chem.* **1978**, *179*, 2837.

(2) Soga, K.; Imai, E.; Hattori, I. *Polym. J.* **1981**, *13*, 407.

(3) (a) U.S. Patent 4,943,677, 1990, to A. Rokicki, Air Products and Chemicals, Inc., and Arco Chemical Co. (b) U.S. Patent 5,026,676, 1991, to S. Motika, Air Products and Chemicals, Inc., Arco Chemical Co., and Mitsui Petrochemical Industries Ltd.

(4) Darensbourg, D. J.; Holtcamp, M. W.; Reibenspies, J. H. *Polyhedron* **1996**, *15*, 2341.

(5) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577.

(6) (a) Kuran, W.; Listos, T. *Macromol. Chem. Phys.* **1994**, *195*, 977. (b) Koinuma, H.; Hirai, H. *Makromol. Chem.* **1977**, *178*, 1283. (c) Lednor, P. W.; Rol, N. C. *J. Chem. Soc., Chem. Commun.* **1985**, 598.

(7) Darensbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 538.

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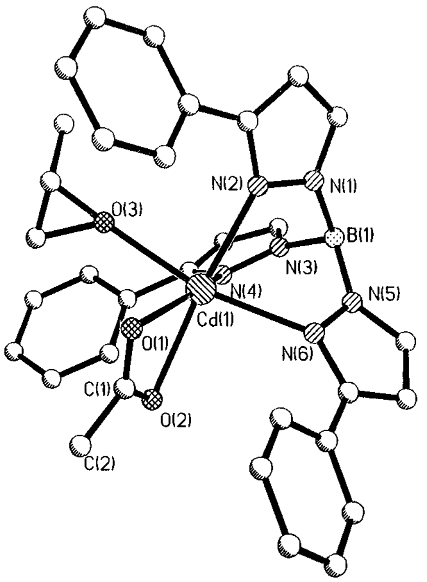

Figure 1. Ball-and-stick representation of complex **2**.

use of pyrazolylborate ligands.[7] These novel complexes, which contained either propylene oxide (PO) or cyclohexene oxide (CHO) coordinated to the metal center, could be thought of as isolated models for this initiation step. A molecular representation of the propylene oxide adduct is depicted in Figure 1. The zinc pyrazolylborate carboxylate analog is four-coordinate, containing a monodentate-bound carboxylate ligand, and does not bind an additional base. Presently we wish to report the synthesis and structures of additional $[\mathrm{Tp^R}]\mathrm{Cd^{II}}$ carboxylates ($[\mathrm{Tp^R}]$ = tris(3-R-pyrazolyl)hydroborate; R = Ph, ^{t}Bu), some of which coordinate donor solvents and epoxides. Methylene chloride solutions of the sterically less encumbered carboxylate complexes of cadmium (R = Ph) in the presence of cyclic ethers or thioethers have been shown to comprise a rapid equilibrium between five-coordinate and six-coordinate species (eq 1).

$$[\mathrm{Tp^{Ph}}]\mathrm{Cd(acetate)} + \mathrm{ether} \rightleftharpoons [\mathrm{Tp^{Ph}}]\mathrm{Cd(acetate)\cdot ether} \qquad (1)$$

Binding constants for these complexes were determined by taking advantage of the sensitivity of ^{113}Cd NMR spectroscopy to the metal atom environment.[8]

Experimental Section

Methods and Materials. All solvents were freshly distilled before use. Propylene oxide, cyclohexene oxide, and propylene sulfide were freshly distilled over calcium hydride prior to use. $\mathrm{Cd(acetate)_2\cdot 2H_2O}$ and cyanoacetic acid were purchased from Aldrich Chemical Co. and used as received. Acetic acid ($-^{13}$COOH) and sodium acetate ($\mathrm{NaO_2{}^{13}CCH_3}$) were purchased from Cambridge Isotope Laboratories. Potassium hydrotris(3-phenylpyrazol-1-yl)borate and potassium hydrotris(3-*tert*-butylpyrazol-1yl)borate were prepared according to the published procedure.[9] Infrared spectra were recorded on a Mattson 6021 spectrometer with DTGS and MCT detectors. ^{1}H 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 using an external 0.1 M $\mathrm{Cd(ClO_4)_2}$ reference. Elemental analysis were carried out by Galbraith Laboratories Inc.

Caution! Cadmium is a toxic metal! Care should be taken in handling these complexes and in their disposal.

Synthesis of $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(acetate)\cdot THF}$ (1). A THF solution of $\mathrm{KHB(3\text{-}Phpz)_3}$ (1.10 g, 2.30 mmol) was added dropwise to a mixture of excess $\mathrm{Cd(acetate)_2\cdot 2H_2O}$ (0.88 g, 3.20 mmol) in 80 mL of THF. The mixture was stirred an additional 1 h and then filtered. The filtrate was concentrated to 15 mL, and hexane was added to completely precipitate the product. The precipitate was filtered off and dried overnight to give 1.25 g (80% yield) of **1**. Crystals of the product were grown by slow diffusion of hexane into a concentrated THF solution at −20 °C. Anal. Calcd for $\mathrm{C_{33}H_{33}N_6O_3CdB}$: C, 57.87; H, 4.86. Found: C, 57.26; H, 4.83. IR (KBr; $\nu(\mathrm{CO_2})$, cm^{-1}): 1543 (s), 1418 (m). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.73 [4H, br {THF}], 1.91 [3H, s {Cd−O$_2$C*CH$_3$*}], 3.63 [4H, br {THF}], 6.48 [3H, d (η^3-HB(3-Ph*pz*)$_3$−Cd}], 7.4−7.7 [15H, m {η^3-HB(3-*Ph*pz)$_3$−Cd}], 7.82 [3H, d {η^3-HB-(3-Ph*pz*)$_3$−Cd}].

Synthesis of $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(acetate)\cdot PO}$ (2). $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(acetate)\cdot THF}$ (0.5 g) was dissolved in a minimum amount of $\mathrm{CH_2Cl_2}$. Toluene, twice the amount of the $\mathrm{CH_2Cl_2}$, was added to the solution, and all solvent was then removed under vacuum. This process was repeated several times until all THF was removed from the solid, as determined by ^{1}H NMR. The solid was then dissolved in propylene oxide, the solution was filtered through Celite, and the propylene oxide was removed under vacuum. The yield was nearly quantitative. Crystals of **2** were grown by slow diffusion of hexane into a propylene oxide solution of **2**. Anal. Calcd for $\mathrm{C_{32}H_{31}N_6O_3CdB}$: C, 57.29; H, 4.66. Found: C, 56.14; H, 4.69. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.30 [3H, d {*CH$_3$*CHCH$_2$O}], 1.91 [3H, s {Cd-O$_2$C*CH$_3$*}], 2.41 [1H, q {CH$_3$CH*CH$_2$*O}], 2.75 [1H, t {CH$_3$-CH*CH$_2$*O}], 2.95 [1H, m {CH$_3$*CH*CH$_2$O}], 6.48 [3H, d {η^3-HB(3-Ph*pz*)$_3$−Cd}], 7.4−7.7 [15H, m {η^3-HB(3-*Ph*pz)$_3$−Cd}], 7.82 [3H, d {η^3-HB(3-Ph*pz*)$_3$−Cd}].

Synthesis of $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{(II)}(acetate)\cdot CHO}$ (3), $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(acetate)\cdot PS}$ (PS = Propylene Sulfide) (4), and $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(acetate)\cdot diox}$ (diox = Dioxane) (5). These complexes were synthesized in a manner analogous to that for **2**. The spectroscopic data for **3**−**5** are identical to those of **2**, with exception of those for the respective ether or thioether ligand.

Synthesis of $[\mathrm{Tp^{Bu}}]\mathrm{Cd^{II}(acetate)}$ (6).[10] KHB(3-Bu^{t}pz)$_3$ (1.00 g, 2.38 mmol) and a slight excess of $\mathrm{Cd(acetate)_2\cdot 2H_2O}$ (0.70 g, 2.63 mmol) were stirred together in 30 mL of THF for 3 h. The THF was removed under vacuum, and benzene was added to extract the product. The benzene solution was filtered, and the solvent was removed under vacuum to give the product. The solid was washed with hexane and dried overnight under vacuum to given 0.79 g (60% yield) of white powder. Crystals were grown by cooling a concentrated THF solution of **6** at −20 °C for several hours. Anal. Calcd for $\mathrm{C_{23}H_{37}N_6O_2CdB}$: C, 49.97; H, 6.75. Found: C, 48.74; H, 6.75. IR ($\mathrm{CH_2Cl_2}$; $\nu(\mathrm{CO_2})$, cm^{-1}): 1547 (s), 1439 (m). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.34 [27H, s {η^4-HB(3-*Bu^t*pz)$_3$−Cd}], 7.55 [3H, d {η^3-HB(3-Bu^t*pz*)$_3$−Cd}].

Synthesis of $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(O_2{}^{13}CCH_3(50\%))\cdot CHO}$. The nonlabeled complex **3** (0.2 g) was placed in a 50 mL flask. One equivalent of 98% ^{13}C-labeled acetic acid was added with a 10 mL syringe. A 20 mL portion of cyclohexene oxide was added, and the solvent was removed under vacuum. A minimal amount of cyclohexene oxide was added to dissolve the complex, the solution was filtered, and precipitation was induced with hexane. The white precipitate was filtered off, washed with hexane, and dried under vacuum. Approximately 50% incorporation of labeled acetate was observed by infrared spectroscopy and ^{13}C NMR. IR ($\mathrm{CH_2Cl_2}$; $\nu(\mathrm{CO_2})$, cm^{-1}): 1546−1522. ^{13}C NMR ($\mathrm{CDCl_3}$): 180 ppm.

Synthesis of $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(cyanoacetate)\cdot THF}$ (7). $[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}}$-(acetate)·THF (0.5 g) was added to a 50 mL flask with 1 equiv of cyanoacetic acid in 30 mL of THF. The solution was allowed to stir for 2 h and was then concentrated to approximately 5 mL. A 30 mL portion of hexane was added to precipitate the product. The white precipitate was filtered off and washed with 10 mL of $\mathrm{H_2O}$ followed by 10 mL of cold ether. The product was dried overnight under vacuum. Crystals were obtained by cooling a concentrated THF solution of the product. IR (THF; $\nu(\mathrm{CO_2})$, cm^{-1}): 1591 (s), 1404 (s); ν(C−N): 2257 (w).

^{113}Cd NMR Experiments. Samples were made by dissolving approximately 50 mg of compound in 3 mL of $\mathrm{CD_2Cl_2/CH_2Cl_2}$ (1:2).

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(8) (a) Summers, M. F. *Coord. Chem. Rev.* **1988**, *86*, 43−134. (b) Ellis, P. D. In *The Multinuclear Approach to NMR Spectroscopy*; Lamberg, J. B., Riddell, F. G., Eds.; Reidel Publishing Co.: Dordrecht, The Netherlands, 1983; p 457.

(9) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

(10) Reger, D. L.; Meyers, S. M.; Mason, S. S.; Rheingold, A. L.; Haggerty, B. S.; Ellis, P. D. *Inorg. Chem.* **1995**, *34*, 4996.

Table 1. Crystallographic Data and Data Collection Parameters for Complexes **1**, **5**, and **6**

	1	**5**	**6**
formula	$C_{33}H_{33}BCdN_6O_3$	$C_{33}H_{36}BCdN_6O_4$	$C_{35}H_{61}BCdN_6O_5$
fw	684.26	700.22	769.11
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2/n$	$P2_1/n$	$P2_1$
a, Å	11.826(3)	11.849(2)	10.865(2)
b, Å	14.686(4)	14.515(2)	16.720(3)
c, Å	18.229(8)	18.618(2)	11.206(2)
β, deg	103.30(3)	102.993(13)	102.24(3)
V, Å^3	3081(2)	3120.3(8)	1989.4(6)
Z	4	4	2
d (calcd), g/cm^3	1.476	1.490	1.284
abs coeff, mm^{-1}	0.751	0.748	0.594
λ, Å	0.710 73	0.710 73	0.710 73
T, K	193(2)	192(2)	163(2)
R,[a] %	8.32	5.73	6.03
R_w,[a] %	16.66	13.02	15.57

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

The concentration of the Cd complex was calculated by subtracting the amount of $[Tp^{Ph}]_2Cd$ in the sample (determined previously by integration of ^1H NMR). Samples were approximately 0.025 M in Cd carboxylate complex. Spectra were obtained at 15 °C intervals between +20 and −85 °C. After the sample had warmed to room temperature, a 10 mol excess of the ether or thioether was added, and another set of spectra were obtained.

Calculation of Equilibrium Constants. The peak positions for five-coordinate N_3O_2Cd (δ_F) at room temperature and six-coordinate N_3O_3-Cd (δ_C) at −85 °C with excess ether were determined and used to calculate the percentage of six-coordinate complex (α) present at temperatures between the two extremes through the following relation:

$$\delta = \delta_C(\alpha) + \delta_F(1 - \alpha) \qquad \delta = \text{experimental shift}$$

The equilibrium constant at each temperature was calculated in the following way:

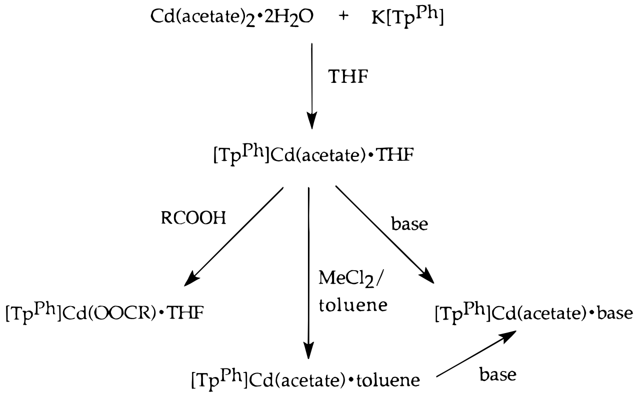
$$K = \alpha[\text{Cd complex}]_{\text{init}}/\{([\text{Cd complex}]_{\text{init}} - \alpha[\text{Cd complex}]_{\text{init}})([\text{ether}]_{\text{init}} - \alpha[\text{Cd complex}]_{\text{init}})\}$$

The thermodynamic parameters were determined by plotting ln K vs $1/T$ and calculating the constants from the slope ($-\Delta H/R$) and y intercept ($\Delta S/R$) of the line. Error analysis was carried out by using a program based on the method of least-squares curve-fitting described by Perrin.[11]

High-Pressure Experiments. A typical run consisted of the following procedure. Catalyst (0.1 g) was loaded into the high-pressure reactor apparatus and dried under vacuum at 40 °C overnight. Propylene oxide (10 mL) and dichloromethane (20 mL) were added to the reactor at room temperature through an inlet port. The reactor was pressurized with CO_2 at 1100 psi. The temperature was raised to 130 °C, which raised the total pressure to 2500 psi. The reactor was allowed to run for 18 h. After cooling, the solution was examined by infrared and ^1H NMR spectroscopy.

X-ray Crystallographic Study of 1, 5, and 6. Crystal data and details of the data collections are given in Table 1. Colorless blocks of **1**, **5**, and **6** were mounted on a glass fiber with epoxy cement at room temperature. **1** and **5** were cooled to 193 K and **6** was cooled to 163 K in a N_2 cold stream. Preliminary examination and data collection were performed on a Nicolet R3m/v X-ray diffractometer for **1**, a Siemens P4 X-ray diffractometer for **5**, and a Rigaku AFC5 X-ray diffractometer for **6** (Mo Kα λ = 0.710 73 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 $4.0° \leq 2\theta \leq 50.0°$. Three control reflections collected 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 5604 reflections for **1**, 2293 reflections for **5**, and 3638 reflections for **6**. A semiempirical absorption correction was applied to all complexes. Totals of 5425 unique reflections for **1**, 2189 for **5**, and 3638 for **6** with $|I| \geq 2.0\sigma_I$ 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 $R = 0.0832$, $R_w(F^2) = 0.1666$, and $S = 1.051$ at convergence for **1**, $R = 0.0573$, $R_w(F^2) = 0.1302$, and $S = 1.075$ for **5**, and $R = 0.0603$, $R_w(F^2) = 0.1557$, and $S = 1.117$ for **6**. Hydrogen atoms were placed in 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*.

Scheme 2



Results and Discussion

Synthesis and Structural Studies. The complex $[Tp^{Ph}]Cd^{II}$-(acetate)·THF, **1**, can easily be prepared by reacting the potassium salt of the ligand with a slight excess of $Cd(acetate)_2 \cdot 2H_2O$. It was necessary to carry out the reaction in a large volume of THF to keep the product in solution. Moreover, slow addition of a solution of the salt of the ligand, $KHB(3\text{-}Phpz)_3$, is required to reduce formation of the very stable bis ligand derivative, $[Tp^{Ph}]_2Cd$. Nevertheless, complex **1** undergoes a ligand redistribution reaction in weakly or noncoordinating solvents to afford small quantities of this symmetric complex. This latter derivative has been fully characterized in solution and in the solid-state, as previously described.[12]

Analysis of **1** in chloroform or methylene chloride solution by ^1H and ^{113}Cd NMR indicated that the THF dissociates from the metal center at room temperature. Because of its lability, THF was easily displaced with excess epoxides, and the crystal structures of the propylene oxide, **2**, and cyclohexene oxide, **3**, adducts have been communicated.[7] These complexes were synthesized by repeatedly washing **1** with the corresponding epoxide until the THF was completely replaced; however, large percentages of $[Tp^{Ph}]_2Cd$ are often formed as a side product by this method, since the epoxides are only weakly coordinating solvents. It was later found that, by first washing **1** with methylene chloride and toluene, we could isolate a toluene solvate while minimizing the amount of CdL_2 formed. Unlike THF, toluene can be removed by placing the solid under vacuum for several days. Other Lewis base adducts can be simply prepared by dissolving this toluene solvate in the appropriate ether or thioether and drying in vacuo. In this manner, complexes **2** and **3** were synthesized, as well as a propylene

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(11) Perrin, C. L. *Mathematics for Chemists*; Wiley-Interscience: New York, 1970; p 161.

(12) (a) Reger, D. L.; Meyers, S. M.; Mason, S. S.; Darensbourg, D. J.; Holtcamp, M. W.; Reibenspies, J. H.; Lipton, A. S.; Ellis, P. D. *J. Am. Chem. Soc.* **1995**, *117*, 10998. (b) Reibenspies, J. H.; Klausmeyer, K. K.; Niezgoda, S. A.; Holtcamp, M. W.; Darensbourg, D. J. *Z. Kristallogr.* **1995**, *210*, 617.

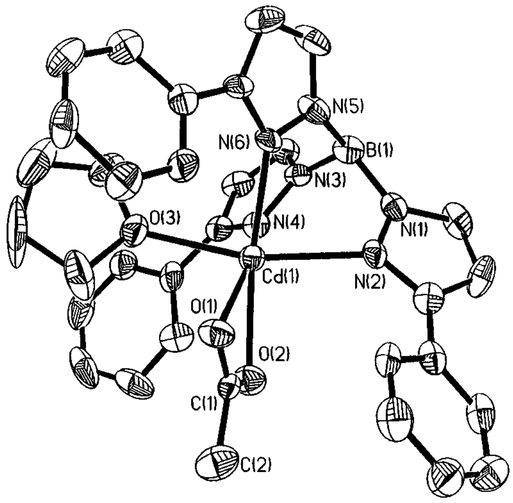

Figure 2. Thermal ellipsoid drawing of complex **1** (50% probability).

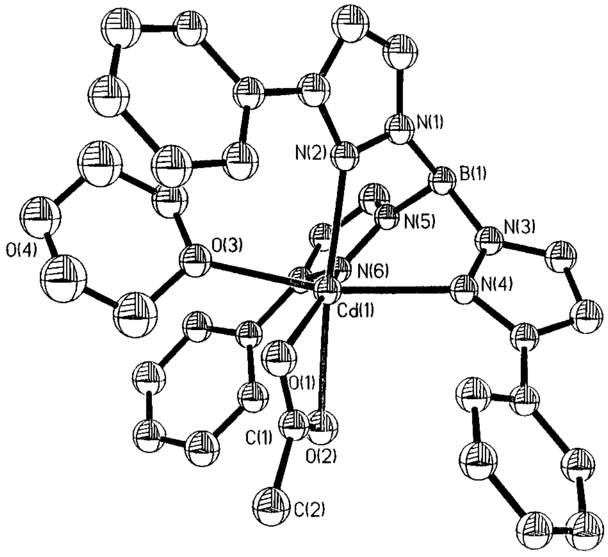

Figure 3. Thermal ellipsoid drawing of complex **5** (50% probability).

sulfide adduct, **4**, and a dioxane adduct, **5**. It is also possible to substitute the acetate ligand upon reaction of complex **1** with 1 equiv of a carboxylic acid which is a stronger acid than acetic acid, e.g., cyanoacetic acid. Scheme 2 summarizes the general approach employed in the synthesis of the complexes under discussion.

Complexes **1** and **5** have been characterized crystallographically, and their structures are shown in Figures 2 and 3, respectively. Selected interatomic bond lengths and bond angles for complexes **1**, **2**, **3**, and **5** are displayed in Table 2. Complex **4** has not yet been structurally defined in the solid state because attempts to crystallize **4** have led to homopolymerization of monomer (*vide infra*). The [Tp^{Ph}] complexes thus far delineated all display distorted octahedral geometry with very similar Cd−O and Cd−N bond lengths. The average Cd−N bond length for these complexes is unexceptional at approximately 2.34 Å.[10] The carboxylate is bound only slightly asymmetrically in all four complexes, with the average difference between the two Cd−O bond lengths being approximately 0.05 Å. The Cd−O_{ether} bond lengths also lie in a small range. The Cd−epoxide bond lengths are very close, 2.414(4) and 2.395 Å for **2** and **3**, respectively. Cd−THF, 2.388(8) Å, is slightly shorter; however the Cd−dioxane bond length, 2.448(7) Å, is the longest, presumably due to steric interactions, but it is shorter than that reported for a Cd−porphyrin structure which was axially coordinated by two dioxane molecules.[13]

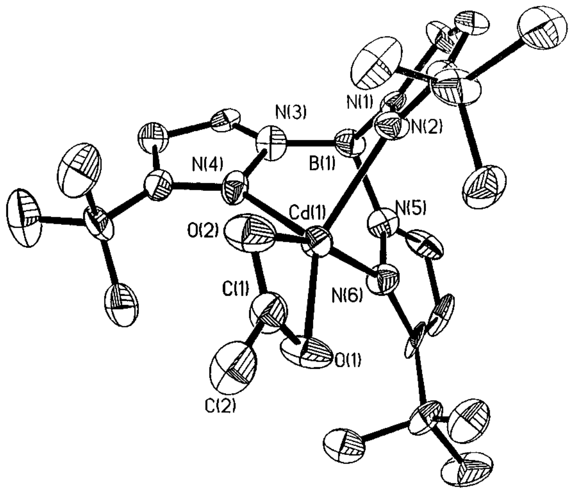

Figure 4. Thermal ellipsoid drawing of complex **6** (50% probability).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) in Complexes **1**−**3** and **5**

[Tp^{Ph}]Cd(acetate)·THF **(1)**			
Cd(1)−O(1)	2.307(8)	Cd(1)−N(2)	2.397(9)
Cd(1)−O(2)	2.342(8)	Cd(1)−N(4)	2.323(9)
Cd(1)−O(3)	2.388(8)	Cd(1)−N(6)	2.321(8)
O(1)−C(1)−O(2)	123.0(11)	O(3)−Cd(1)−N(2)	164.7(3)
O(1)−Cd(1)−O(2)	56.0(3)	N(4)−Cd(1)−O(2)	104.1(3)
O(1)−Cd(1)−N(6)	115.4(3)	N(6)−Cd(1)−N(4)	86.5(3)
[Tp^{Ph}]Cd(acetate)·PO **(2)**			
Cd(1)−O(1)	2.309(3)	Cd(1)−N(6)	2.380(4)
Cd(1)−O(2)	2.355(3)	Cd(1)−N(2)	2.312(4)
Cd(1)−O(3)	2.414(4)	Cd(1)−N(4)	2.321(4)
O(1)−C(1)−O(2)	119.7(4)	N(4)−Cd(1)−O(2)	104.33(11)
O(1)−Cd(1)−O(2)	56.06(11)	O(3)−Cd(1)−N(6)	164.46(14)
O(1)−Cd(1)−N(2)	115.66(12)	N(2)−Cd(1)−N(4)	86.35(12)
[Tp^{Ph}]Cd(acetate)·CHO **(3)**			
Cd(1)−O(1)	2.306(4)	Cd(1)−N(2)	2.325(4)
Cd(1)−O(2)	2.345(4)	Cd(1)−N(4)	2.384(5)
Cd(1)−O(3)	2.395(4)	Cd(1)−N(6)	2.331(4)
O(1)−Cd(1)−O(2)	56.0(2)	N(2)−Cd(1)−O(1)	114.7(2)
O(1)−C(1)−O(2)	123.0(6)	N(2)−Cd(1)−N(6)	87.6(2)
O(2)−Cd(1)−N(6)	103.5(2)	O(3)−Cd(1)−N(4)	165.3(2)
[Tp^{Ph}]Cd(acetate)·diox **(5)**			
Cd(1)−O(1)	2.305(7)	Cd(1)−N(2)	2.319(9)
Cd(1)−O(2)	2.344(9)	Cd(1)−N(4)	2.316(10)
Cd(1)−O(3)	2.448(7)	Cd(1)−N(6)	2.383(9)
O(1)−Cd(1)−O(2)	121.1(13)	O(3)−Cd(1)−N(6)	165.2(3)
O(1)−Cd(1)−O(2)	55.8(3)	N(2)−Cd(1)−N(4)	87.2(3)
O(1)−Cd(1)−N(4)	114.3(3)	N(2)−Cd(1)−O(2)	104.6(30

Soluble cadmium carboxylates were also synthesized using a sterically more demanding pyrazolylborate ligand, tris(3-*tert*-butylpyrazolyl)hydroborate. [Tp^{Bu}]Cd(acetate), **6**, was prepared by the published procedure[10] and characterized in the solid-state by X-ray crystallography. Our intention was to synthesize a complex analogous to **1** which would not be able to form the bis complex, [Tp^{Bu}]$_2$Cd, on the basis of steric considerations. The bulky ligand, however, not only inhibited formation of the bis complex but also prevented coordination of THF as shown in the structure of **6**, depicted in Figure 4, although three THF molecules were found in the crystal lattice of the complex. Selected interatomic bond lengths and bond angles are listed in Table 3. The bulkier ligand also forces the carboxylate to be more asymmetrically bound as compared to those in the [Tp^{Ph}]

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(13) Rodesiler, P. F.; Griffith, E. H.; Ellis, P. D.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1980**, 493.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in $[\mathrm{Tp^{Bu}}]$Cd(acetate) (**6**)

Cd(1)−O(1)	2.211(7)	Cd(1)−N(6)	2.311(7)
Cd(1)−N(4)	2.23(2)	Cd(1)−O(2)	2.369(7)
Cd(1)−N(2)	2.29(2)		
O(1)−Cd(1)−O(2)	56.4(3)	O(1)−Cd(1)−N(2)	134.1(8)
O(1)−C(1)−O(2)	119.5(9)	O(1)−Cd(1)−N(6)	109.4(3)
O(2)−Cd(1)−N(6)	165.7(3)	N(4)−Cd(1)−N(2)	90.5(3)
O(1)−Cd(1)−N(4)	132.2(9)	O(2)−Cd(1)−N(4)	105.7(8)

complexes. The Cd−O(1) and Cd−O(2) bond distances in **6** are 2.211(7) and 2.369(7) Å, respectively ($\Delta l = 0.158$ Å), whereas Δl for **1** is 0.035 Å. The binding mode of the acetate can also be compared with that of the bidentate nitrate in $[\eta^3$-3-^{t}Bu-5-Mepz)$_3$]Cd(η^2-O_2NO), which has Cd−O bond lengths of 2.272(6) and 2.295(7) Å ($\Delta l = 0.023$ Å).[14] The Zn(II) analog of **6**, on the other hand, has been shown to have a monodentate-bound carboxylate group.[15]

The acetate group of **1** was exchanged by reacting **1** with carboxylic acids to synthesize other carboxylates. In this manner, we were able to prepare a ^{13}C-labeled carboxylate, $[\mathrm{Tp^{Ph}}]\mathrm{Cd(O_2{}^{13}CCH_3(50\%))\cdot PO}$. Similarly, it was possible to prepare $[\mathrm{Tp^{Ph}}]$Cd(cyanoacetate)·THF, **7**, by this route. An X-ray crystal structure of this complex, which was published previously, again revealed bidentate coordination of the carboxylate.[16] This contrasts with cyanoacetate complexes of Zn(II) and Cu(I), first-row d^{10} metals, whose carboxylate groups are coordinated monodentately.[17] The Cd−O(1) and Cd−O(2) bond distances are 2.386(5) and 2.354 Å ($\Delta l = 0.032$ Å), respectively, and the Cd−O_{THF} bond distance is 2.386(5) Å. The average Cd−N bond distance is 2.330(5) Å. A third carboxylate complex, $[\mathrm{Tp^{Ph}}]$Cd(fumarate), was synthesized by the same method and characterized crystallographically but will be discussed elsewhere.

Solution Studies. At ambient temperature in chloroform or dichloromethane, complex **1** displays a single resonance in its ^{113}Cd NMR spectrum at 150 ppm relative to $\mathrm{Cd(ClO_4)_2}$, indicating the predominance of the dissociated five-coordinate $\mathrm{N_3O_2Cd}$ complex (eq 2).[10,16] This peak is observed to shift

$$\underset{\delta\,(^{113}\mathrm{Cd}) = 156\ \mathrm{ppm}}{[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(acetate)}} + \mathrm{THF} \overset{K_{eq}}{\rightleftharpoons} \underset{\delta\,(^{113}\mathrm{Cd}) = 83\ \mathrm{ppm}}{[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}acetate{\cdot}THF}} \qquad (2)$$

upfield to 83 ppm as the temperature is lowered to −90 °C and/or if excess THF is present (see Figure 5). Under these conditions, the rapid equilibrium in eq 2 shifts to the right, enhancing the concentration of the saturated six-coordinate cadmium(II) complex. Similarly, complexes **2**−**5** in dichloromethane at room temperature display a common ^{113}Cd resonance at 156 ppm, corresponding to complete dissociation of the cyclic ether or thioether to provide the five-coordinated species. This observation is consistent with the latter ligands being less basic than THF. At −90 °C in the presence of excess ether, the saturated six-coordinate complexes provide ^{113}Cd signals shifted upfield near 85 ppm. The ^{113}Cd NMR peak positions for all complexes are listed in Table 4. The results for **5** were significant since the Cdporphyrin·2(diox) complex mentioned previously showed very little change in its ^{113}Cd NMR spectrum when excess dioxane was added to a solution of the Cd porphyrin, although the crystal structure contained two weakly coordinated dioxane molecules.[13]

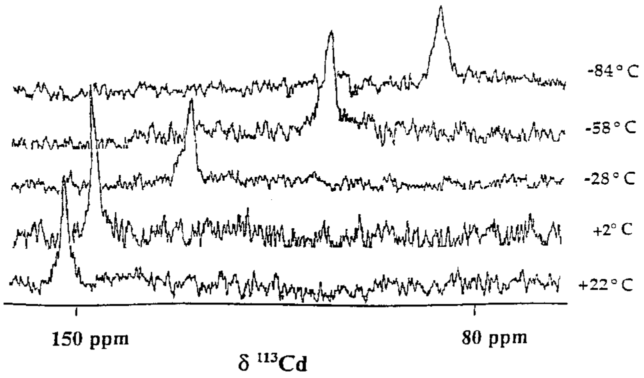

Figure 5. Variable-temperature ^{113}Cd NMR spectra of complex **1** in CD_2Cl_2. The [Cd]/[THF] molar ratio is 1/1 for spectra at 22, 1.8, and −28 °C for 1/10 for spectra at −58 and −84 °C.

Table 4. ^{113}Cd NMR Peak Postions Observed for Complexes in CD_2Cl_2

complex	δ, ppm 22 °C	 excess base, −88 °C
$[\mathrm{Tp^{Ph}}]$Cd(acetate)·THF (**1**)	152	82
$[\mathrm{Tp^{Ph}}]$Cd(acetate)·PO (**2**)	156	82
$[\mathrm{Tp^{Ph}}]$Cd(acetate)·CHO (**3**)	156	82
$[\mathrm{Tp^{Ph}}]$Cd(acetate)·PS (**4**)	157	113
$[\mathrm{Tp^{Ph}}]$Cd(acetate)·diox (**5**)	155	83
$[\mathrm{Tp^{Ph}}]$Cd(acetate)·tol	156	156
$[\mathrm{Tp^{Ph}}]$Cd(acetate)·3-Me-BO	156	156
$[\mathrm{Tp^{Bu}}]$Cd(acetate) (**6**)[a]	146	146

[a] Excess THF was added to solutions of **6**.

The binding of THF and epoxides to the Cd(II) metal center can also be monitored *via* ^{1}H NMR spectroscopy. For example, the spectrum of **1** at room temperature in chloroform shows two multiplets at 3.63 and 1.73 ppm, indicative of free THF. These resonances shift upfield as the temperature is lowered, which is characteristic of THF binding. Additionally, when an equimolar amount of propylene oxide is mixed with **1** and the temperature lowered, the THF multiplets again shift upfield while the propylene oxide peaks remain in the same positions. Through a series of variable-temperature ^{1}H NMR competition studies of **1** or **2** in the presence of an approximately equimolar amount of epoxide, propylene sulfide, dioxane, or THF, a relative order of thermodynamic selection for binding to the Cd(II) center has been determined: THF > dioxane > propylene sulfide > cyclohexene oxide ≥ propylene oxide.

Thermodynamic constants for the equilibrium in eq 2 were calculated from variable-temperature ^{113}Cd NMR experiments, according to the method of Popov.[18] Because the peak positions for the five-coordinated complex at room temperature (156 ppm) and the six-coordinate complex at −84 °C (83 ppm) were determined, it can be assumed that intermediate peak positions are directly proportional to the percentage of each present. The spectra were collected at temperatures between the two extremes for samples in which the initial concentrations of cadmium complex and Lewis base were known. The concentrations of both complexes, as well as values for the equilibrium constant, K, were then calculated as a function of temperature from the peak positions. Plotting ln K vs T^{-1} allowed calculation of the enthalpy, entropy, and free energy of the equilibrium defined

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(14) Looney, A.; Saleh, A.; Zhang, Y.; Parkin, G. *Inorg. Chem.* **1994**, *33*, 1158.

(15) Looney, A.; Han, R.; Gorrell, I. B.; Cornbise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274.

(16) Reibenspies, J. H.; Holtcamp, M. W.; Khandelwal, B.; Darensbourg, D. J. *Z. Kristallogr.* **1995**, *210*, 146.

(17) Darensbourg, D. J.; Holtcamp, M. W.; Longridge, E. M.; Khandelwal, B.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 318.

(18) Roach, E. T.; Hardy, P. R.; Popov, A. I. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 359.

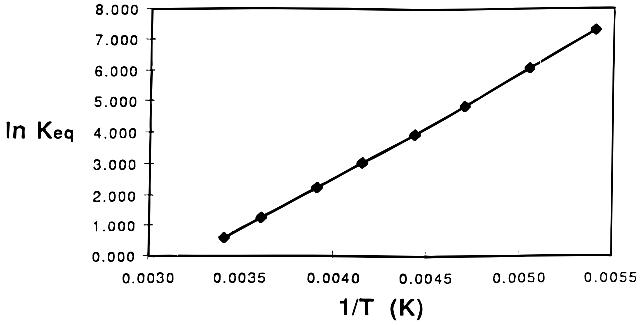

Figure 6. Plot of K_{eq} as a function of temperatur for complex **1** at a [Cd]/[base] ratio of 1.

Table 5. Calculated Thermodynamic Parameters for the Reaction Defined in Eq 2[a]

adduct	$\Delta H°$, kJ/mol	$\Delta S°$, J/(K mol)	$\Delta G°$, kJ/mol	K (298 K)
THF	−27.7 ± 0.2	−89.7 ± 0.7	−1.00 ± 0.16	1.479
dioxane	−26.2 ± 0.4	−88.4 ± 1.6	+0.184 ± 0.6	0.928
propylene sulfide	−24.7 ± 1.0	−88.5 ± 4.5	+1.67 ± 1.04	0.509
cyclohexene oxide	−24.7 ± 1.0	−95.4 ± 4.2	+3.73 ± 1.00	0.222
propylene oxide	−24.3 ± 1.4	−94.1 ± 5.7	+3.74 ± 1.35	0.221

[a] Data used for calculations were taken from 1 mol/10 mol [Cd]/[base] samples.

in eq 2. The values of K at 22 °C, $\Delta H°$, $\Delta S°$, and $\Delta G°$ for the Lewis bases studied are summarized in Table 5. The relative order of binding of donor solvents is the same as that found in ^{1}H NMR competitive studies previously discussed. Furthermore, this binding order is comparable to that found in a study by Dumas in which the formation constants for a series of Cd(II)−porphyrin oxirane and thiirane complexes were calculated through UV−visible experiments, although some values for K vary from those reported.[19] Alternatively, when the interaction of $ZnEt_2$ with some of these name Lewis bases was studied, PO was found to bind better than PS, though THF still showed greater complex-forming ability.[20]

Variable-temperature ^{113}Cd NMR experiments were also performed for 2,3-dimethylbutene oxide and toluene. Each displayed a single peak at ambient temperature in the ^{113}Cd NMR at approximately 156 ppm for the five-coordinate Cd. For both solvates, no change in peak position was seen after lowering the temperature or after adding excess base; thus these potential donor molecules do not coordinate to the metal center. These results were expected for toluene, but failure of the bulky, more electron-donating epoxide ligand to bind is presumed to be due to steric interactions. Because there is no change in the NMR spectra with temperature, these experiments prove that the resonance at 156 ppm is due to the five-coordinate [Tp^{Ph}]Cd(acetate) complex and that this peak position is not very temperature-dependent.

A ^{113}Cd spectrum of **6** in dichloromethane at room temperature showed one resonance at 145 ppm relative to $Cd(ClO_4)_2$, which is very close to the previously reported peak position.[10] When the solution was cooled to −90 °C in the presence of excess THF or propylene sulfide, only a very slight shift (less than 5 ppm) was noticed. This indicates that there is no interaction of the cadmium center with THF or the thiirane, as would be expected on the basis of the solid state structure. Thus, although the bulkier ligand prevents the formation of the L_2Cd byproducts, it also renders the complex useless for epoxide-binding studies.

While the majority of our studies have centered around the lability of the epoxide ligand, we have also studied the exchange reaction of the acetate ligand. It was found that, by stirring the complex [Tp^{Ph}]Cd(acetate)·THF or [Tp^{Bu}]Cd(acetate) dissolved in methylene chloride with a slurry of 1 equiv of $NaO_2{}^{13}CCH_3$, it was possible to prepare the corresponding ^{13}C-labeled acetate derivatives. The ^{13}C NMR spectra of these complexes in chloroform-d_1 solution exhibited greatly enhanced, relative to the ^{13}C-natural-abundance spectra, signals at 180 ppm due to the acetate ligand. On the other hand, the free acetate ligand exhibited a carbon resonance upfield of this signal at 176 ppm. Alternatively, it is possible to prepare the ^{13}C-labeled acetate complexes *via* the reaction previously reported for the CHO derivative employing ^{13}C-labeled acetic acid as indicated in eq 3.[7]

$$[\mathrm{Tp^{Ph}}]\mathrm{Cd(acetate)\cdot CHO} + \mathrm{CH_3{}^{13}COOH} \rightarrow [\mathrm{Tp^{Ph}}]\mathrm{Cd(O_2{}^{13}CCH_3)\cdot CHO} + \text{acetic acid} \quad (3)$$

In order to qualitatively assess the rate of exchange of bound acetate with free acetate ion in solution, we examined a chloroform-d_1 solution of kryptofix-221-solubilized $NaO_2{}^{13}CCH_3$ and unlabeled [Tp^{Bu}]Cd(acetate) by ^{13}C NMR spectroscopy. The sterically encumbered complex **6** was chosen for this study since it was demonstrated that the five-coordinate cadmium center does not interact with a sixth ligand (*vide supra*). Hence, this derivative should be best suited for examining the rate of dissociative acetate exchange. Upon addition of **6** to [Na(kryptofix-221)][$O_2{}^{13}CCH_3$] at ambient temperature, the ^{13}C signal arising from free acetate at 176 ppm decreased in intensity significantly with a concomitant increase in intensity of the ^{13}C resonance representing the bound acetate ligand. Both NMR signals were considerably broadened relative to the corresponding peaks for the individual components, indicative of rather fast exchange. Further indication of chemical exchange was noted in the ^{1}H NMR spectrum of this reaction mixture where the proton resonance for the bound acetate ligand at 2.22 ppm shifted toward the resonance of the free ligand at 1.91 ppm and broadened considerably. Thus, the reaction defined in eq 4 occurs readily at ambient temperature. We cannot rule out an intermediate in this carboxylate exchange process which involves both incoming and departing acetate ligands, each bound in a monodentate fashion to the metal center. However, such a mechanism for exchange is unlikely due to the low concentration of incoming ligand (2-fold excess)[21] and the steric crowding which exists about the cadmium center.

$$[\mathrm{Tp^{Bu}}]\mathrm{Cd(acetate)} + \mathrm{O_2{}^{13}CCH_3{}^-} \rightleftharpoons [\mathrm{Tp^{Bu}}]\mathrm{Cd(O_2{}^{13}CCH_3)} + \mathrm{(acetate)^-} \quad (4)$$

Model Catalytic Studies. Although the complexes reported herein were designed to model the active site of carbon dioxide−epoxide copolymerization catalysts, they themselves are not active catalysts for the synthesis of polycarbonates. Nevertheless, these complexes do mimic the proposed initiation step in polycarbonate formation. This process involves ring opening of the metal-bound epoxide by the carboxylate ligand (Scheme 1). Subsequent steps including oligomerization of the epoxide *via* a series of epoxide-ring-opening reactions (eq 5). If the process is carried out in the presence of carbon dioxide, cyclic carbonate production, an alternative reaction route during polycarbonate synthesis, is the dominant reaction pathway (eq 6).

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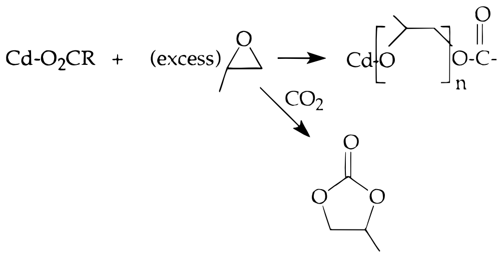
(19) Dumas, P.; Guerin, P. *Can. J. Chem.* **1978**, *56*, 925.

(20) Denisov, V. M.; Kuznetsoz, Y. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, *25*, 2595.

(21) It was not possible to carry out the exchange reaction in a larger excess of incoming acetate ligand.

(22) Similar activity has been seen for dialkylaluminum catalysts: Backsai, R. *J. Polym. Sci.* **1963**, *A1*, 2777.

(23) Cooper, W.; Morgan, D. R.; Wragg, R. T. *Eur. Polym. J.* **1969**, *5*, 71.



(5)

(6)

We previously reported that when a cyclohexene oxide solution of $[Tp^{Ph}]Cd(O_2{}^{13}CCH_3)\cdot CHO$ is refluxed, oligomerization of CHO occurs, initiated by ring opening of the epoxide by the acetate group.[7] The resulting oligomers of cyclohexene oxide, with number- and weight-averaged molecular weights of 300 and 1400, respectively, possess a terminal acetate group as verified by ^{13}C NMR spectroscopy. When the five-coordinate complex **6** is refluxed with CHO in methylene chloride for several hours, trace signals of epoxide−carboxylate coupling occur as well.

Additionally, these soluble cadmium carboxylates are even more effective at catalyzing the homopolymerization of thioepoxides. For instance, when the toluene solvate of $[Tp^{Ph}]Cd$(acetate) is stirred at ambient temperature with propylene sulfide, a viscous white polymer begins to form within minutes. This process can be slowed by cooling the reaction mixture below room temperature, conditions under which the monomeric complex **4** was obtained (*vide supra*). On the other hand, cyclohexene sulfide in the presence of the toluene solvate of $[Tp^{Ph}]Cd$(acetate) rapidly polymerized in a very exothermic reaction, even when the mixture was cooled below 0 °C.[22] In comparison, kryptofix-221-solubilized sodium acetate homopolymerized cyclohexene sulfide very slowly at ambient temperature. Cadmium thiolates have been shown to be very active for the homopolymerization of thiiranes,[23] and a coordination polymerization mechanism was proposed for the homopolymerization of styrene sulfide by a cadmium thiolate.[24] It is not anticipated that the copolymerization of thiirane with CO_2 will occur on the basis of studies which utilized Al and Zn catalysts.[25]

The capabilities of these complexes as catalysts for copolymerization were tested by refluxing them in propylene oxide at high pressures of CO_2. Complexes **1** and **2** again yielded small amounts of epoxide−carboxylate-coupled products but also produced catalytic amounts of cyclic carbonate. The five-coordinate complex **6**, which has no epoxide bound to the cadmium, and the $[Tp^{Ph}]_2Cd$ complex were refluxed in propylene oxide under identical conditions, and they, too, produced catalytic amounts of cyclic carbonate. Thus, epoxide−carboxylate coupling at the metal center is not necessary for cyclic carbonate formation under these conditions. An active catalytic species may instead form by acetate and/or hydroborate ligand dissociation from the metal.

Conclusions

Herein we have described the synthesis and characterization of several soluble (tris(pyrazolyl)hydroborato)cadmium carboxylate adducts of cyclic ethers and thioethers. These six-coordinate derivatives are very labile with regard to ether dissociation, with ether binding noted only in the solid state or at low temperature in solution. The steric requirements of the ancillary tris(3-R-pyrazolyl)hydroborate ligand are extremely important in that it is necessary for this ligand to be large enough to minimize bis(tris(3-R-pyrazolyl)hydroborato)cadmium formation yet to be of appropriate size to allow ether coordination. This was clearly demonstrated here, for the $[Tp^{Ph}]Cd$(acetate) complex readily afforded six-coordinate complexes with ethers with minimal formation of $[Tp^{Ph}]_2Cd$, whereas, the $[Tp^{Bu}]Cd$(acetate) derivative crystallized from THF solution as a five-coordinate derivative with THF in the crystal lattice.

Solid-state structural characterization of the THF, propylene oxide, cyclohexene oxide, and dioxane derivatives of $[Tp^{Ph}]Cd$(acetate) revealed the Cd−O bond distances to the ether ligand to vary over the narrow range 2.388(8) Å (THF) to 2.448(7) Å (dioxane) with a slightly asymmetrically chelated carboxylate group (average ΔCd−O = 0.040[3] Å for Cd−acetate bonds). Similarly, in solution, the equilibrium constants for cyclic ether binding (eq 1) at 25 °C span a rather attenuated set of values extending from 1.50 M^{-1} for THF to 0.221 M^{-1} for propylene oxide, with the overall order being THF > dioxane > PS > CHO ≥ PO. The corresponding thermodynamic parameters, $\Delta H°$ and $\Delta S°$, were found to cover the ranges −27.7 to −24.3 kJ/mol and −89.7 to −94.1 J/(mol K), respectively, for the boundary cases cited above.

Although these epoxide complexes have been shown to serve as excellent models for the initiation step in the copolymerizaion of epoxides with carbon dioxide catalyzed by metal carboxylates, they themselves are not effective as copolymerization catalysts. That is, the carboxylate ligand was found to ring-open the epoxide, leading to a metal alkoxide which can further react with the epoxide to provide polyether oligomers with ester end groups. A similar, more rapid oligomerization process occurred when the analogous reaction was carried out with cyclohexene sulfide, where the C−S bond is weaker than the C−O bond. Relevant to this thioepoxide−carboxylate coupling mechanism, despite the fact that we have demonstrated that the acetate ligand readily exchanges with free acetate in solution, the rate of oligomerization of thioepoxide in the presence of the cadmium complex greatly exceeds the oligomerization process initiated by kryptofix-221-solubilized sodium acetate. Nevertheless, the initial epoxide-ring-opening process could result from free acetate attack of a metal-bound epoxide ligand, leading concomitantly to metal alkoxide formation. By way of contrast, upon addition of carbon dioxide to the cadmium-catalyzed oligomerization reaction, cyclic carbonate formation takes precedence over copolymerization. This is not the case for the active zinc dicarboxylate catalysts which afford high-molecular-weight polycarbonates with little cyclic carbonate production.

Finally, the low selectivity for cyclic ether binding strongly suggests that THF and dioxane would be poor choices of solvent for carrying out epoxide polymerization processes. Indeed, when these solvents are used in the preparation of zinc glutarate catalysts, these catalysts exhibit reduced reactivity.[3b] Furthermore, terpolymerization of epoxides and carbon dioxide would be expected to provide nearly random incorporation of epoxides. Both of these predictions have been realized for the $Zn(OR)_2\cdot$2ether catalyst systems we reported previously.[5]

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Supporting Information Available: Ball-and-stick drawings of the molecular structures with atom labeling for complexes **1**, **5**, and **6** tables of non-hydrogen atomic coordinates and equivalent isotropic thermal parameters, anisotropic atomic coordinates and isotropic thermal parameters for complexes **1**, **5**, and **6** (30 pages). Ordering information is given on any current masthead page.

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(24) Noshay, A.; Price, C. C. *J. Polym. Sci.* **1961**, *54*, 533.

(25) Kuran, W.; Rokicki, A.; Wielgopolan, W. *Makromol. Chem.* **1978**, *179*, 2545.