

¹¹³Cd NMR Determination of the Binding Parameters of Alicyclic Epoxides to [Hydrotris(3-phenylpyrazol-1-yl)borate]Cd(II) Acetate

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The thermodynamic parameters for the binding of a series of epoxides to the complex [hydrotris(3-phenylpyrazol-1-yl)borate]Cd(II) acetate have been determined via ¹¹³Cd NMR spectroscopy. As the activation of an epoxide by interaction with a metal center is a key step in the copolymerization of carbon dioxide and epoxides to produce polycarbonates, the tendency for epoxides to bind to metal centers may play a role in the propensity for epoxides to ring-open. The epoxides examined include (+)-limonene oxide, 1,4-dihydronaphthalene oxide, [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane, *exo*-norbornene oxide, and α -pinene oxide. DFT calculations were performed to give optimized geometries of the epoxide adducts of the cadmium complex. Our investigations show that the binding abilities of these alicyclic epoxides vary over the range -22.1 to -38.7 kJ mol⁻¹ for ΔH^\ddagger and do not differ significantly from the corresponding values previously determined for the easily ring-opened epoxides (cyclohexene oxide and propylene oxide). The optimized geometries give a metal center–epoxide (Cd–O) bond distance range of 2.401–2.448 Å, which is in good agreement with values obtained experimentally for selected derivatives. In addition, comparative studies involving the more strongly binding phosphine and amine ligands are reported. From these observations we conclude that the binding of the epoxide by the metal complex is not necessarily the determining factor in the ability of the epoxide to be ring-opened by a nucleophile.

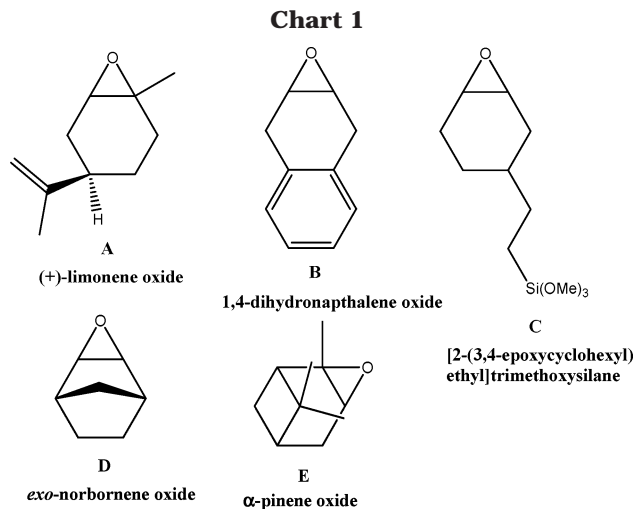
Introduction

Since its initial discovery by Inoue in 1969,¹ interest has increased in the production of polycarbonates via the catalytic coupling of carbon dioxide and epoxides. This process has numerous economical and environmental advantages over the current industrial process for production of polycarbonates including use of the abundant CO₂ molecule as a C1 feedstock and the elimination of hazardous reagents such as phosgene. To date, the most successful studies have involved the production of poly(cyclohexene carbonate) from CO₂ and cyclohexene oxide utilizing zinc-, chromium-, or aluminum-based catalysts.² Our group and others have published studies outlining the substandard physical properties of this polymer as compared to the industri-

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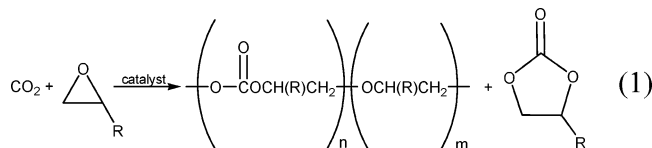


ally produced bisphenol-A polycarbonate.³ We have recently begun to target other epoxides (Chart 1) as potential comonomers for production of more desirable polymer products.⁴ These investigations are focused on epoxides containing a cyclohexyl backbone due to the tendency of cyclohexene oxide to resist formation of

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stable cyclic carbonates, a common byproduct in this reaction (1).



While we have successfully produced copolymer from [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane,^{4b} and to some extent 1,4-dihydronaphthalene oxide,^{4c} we have been unable to generate significant amounts of copolymer from the other targeted epoxides. In many cases we were unable to even ring-open the epoxide, producing epoxide adducts of our zinc-based catalysts.^{4a}

Previous publications have shown that the activation of the epoxide by coordination to the metal center is a key step in the reaction mechanism to produce polycarbonate (Scheme 1).⁵ It is our concern that the propensity of the epoxide to interact with the metal complex should play an important role in the subsequent ring-opening of the substrate. We have previously shown that the thermodynamic parameters for the binding of cyclic ethers and epoxides to a cadmium metal center can be determined via ¹¹³Cd NMR spectroscopy utilizing [hydrotris(3-phenylpyrazol-1-yl)borate]Cd(II) acetate ([Tp^{Ph}]⁻CdOAc) and [Cd(O-2,6-R₂C₆H₃)₂]₂ as models for the NMR inactive zinc copolymerization catalysts; however, these investigations were limited in the number of epoxides examined.^{4a,6} Herein we report our determination of the thermodynamic binding of potential epoxide comonomers, illustrated in Chart 1, to [Tp^{Ph}]⁻CdOAc. In addition we report the binding of common phosphine and amine ligands for comparison purposes. We also detail density functional theory (DFT) calculations of the structures of the epoxide adducts of [Tp^{Ph}]⁻Cd(OAc). From these findings we conclude that the binding ability of the epoxide to the metal center is not necessarily the determining factor in its proclivity toward ring-opening.

Experimental Section

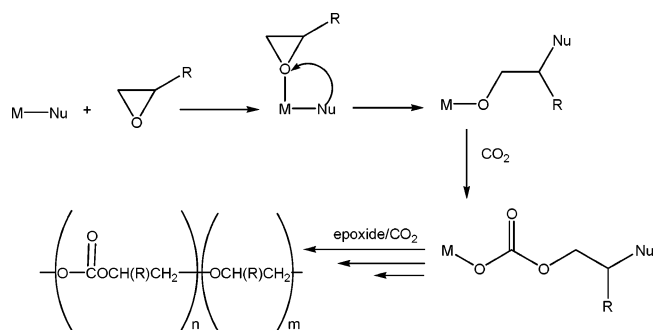
General Procedures. All manipulations were carried out using a combination of Schlenk and glovebox techniques under an inert atmosphere of argon. *Caution! Cadmium is highly toxic! All cadmium wastes should be stored in a separate, labeled container. Use care when handling cadmium!* Tetrahydrofuran, hexanes, and toluene were freshly distilled from sodium benzophenone. Dichloromethane was distilled from P₂O₅. Limonene oxide was purchased from Aldrich, and [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane was purchased from Gelest. Both epoxides were freshly distilled from calcium hydride prior to use. α -Pinene oxide was purchased from Aldrich and distilled onto molecular sieves prior to use. Exonorbene oxide was purchased from Aldrich and used as received. 1,4-Dihydronaphthalene oxide and [hydrotris(3-phenylpyrazol-1-yl)borate]cadmium(II) acetate were prepared according to literature procedures.^{6,7} Ampoules of CD₂Cl₂ were purchased from Cambridge Isotopes.

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Scheme 1



Synthesis of [Tp^{Ph}]⁻Cd(OAc)·piperidine. A 50 mL Schlenk flask is charged under argon with 0.110 g (0.16 mmol) of [Tp^{Ph}]⁻Cd(OAc)·THF. The starting material is converted to [Tp^{Ph}]⁻Cd(OAc)·toluene by repeated dissolutions in 1:2 CH₂Cl₂ and toluene as described in the literature.⁷ The resultant white solid is dissolved in 10 mL of CH₂Cl₂, excess piperidine (0.2 mL, 0.195 g, 2.3 mmol) is added via syringe, and the mixture is stirred for 30 min at room temperature. The solvent is removed under reduced pressure, and the resultant white solid is washed with hexanes (2 × 20 mL), then dried under vacuum. Yield: 0.080 g (72%), white solid. ¹H NMR (CDCl₃): δ 1.01–1.33 [m, 10H, piperidine-CH₂], 1.72 [s, 3H, O₂CCH₃], 2.10 [s, 1H, piperidine-NH], 6.43 [d (*J*_{HH}, 2.2 Hz), 3H, N₂CHCH], 7.35 [t (*J*_{HH}, 7.3 Hz), 3H, phenyl-CH], 7.44 [t (*J*_{HH}, 7.5 Hz), 6H, phenyl-CH₂], 7.73 [d (*J*_{HH}, 7.4 Hz), 6H, phenyl-CH₂], 7.80 [d (*J*_{HH}, 3.0 Hz), 3H, N₂CHCH]. Anal. Calcd for C₃₄H₃₆N₇O₂CdB·CH₂Cl₂: C, 53.70; H, 4.89; N, 12.52. Found: C, 53.57; H, 5.16; N, 12.21.

¹¹³Cd NMR Experiments. NMR samples were prepared by dissolving 0.030 g of the [Tp^{Ph}]⁻Cd(OAc)·toluene compound in 0.75 mL of CD₂Cl₂ in an NMR tube fitted with a rubber septum. One equivalent of liquid epoxide was injected via microsyringe or 1 equiv of solid epoxide was added to the tube with the cadmium compound and dissolved accordingly. ¹¹³Cd NMR spectra were recorded on a Varian 400 MHz broadband NMR spectrometer at temperatures between 20 and –80 °C, in intervals of 10 degrees for each spectrum. ¹H NMR data are not provided for these adducts due to severe overlapping of peaks from the pyrazolyl borate ligand and the various epoxides. After the final spectrum was recorded, the sample was removed from the spectrometer and 10 equiv of epoxide was added via microsyringe, in the case of the liquid epoxides, or by first dissolving in 0.5 mL of CH₂Cl₂ and injecting into the tube via syringe, in the case of the solids. The sample was then reinserted into the spectrometer and an additional spectrum taken at –80 °C.

Computational Details. All DFT calculations were performed using a hybrid functional [the three-parameter exchange functional of Becke (B3)⁸ and the correlation functional of Lee, Yang, and Parr (LYP)] (B3LYP)⁹ as implemented in Gaussian 98.¹⁰ The cadmium and silicon atoms use the effective core potential and associated basis set of Hay and Wadt (LANL2DZ).¹¹ For cadmium the basis set was augmented by the *f* polarization function of Höllwart et al.¹² All geometries are fully optimized and confirmed as minima or *n*-order saddle points by analytical frequency calculations at the same level.

X-ray Crystallography Experiments. X-ray quality crystals of [Tp^{Ph}]⁻Cd(acetate)·piperidine were grown by slow evaporation from a concentrated solution of CD₂Cl₂. Crystals were coated with mineral oil, placed on a glass fiber, and mounted on a Bruker SMART 1000 CCD diffractometer. X-ray data

(8) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

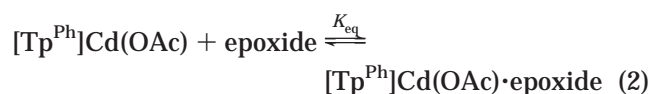
(9) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *37*, 785.

were collected covering more than a hemisphere of reciprocal space by a combination of three sets of exposures. Each exposure had a different φ angle for the crystal orientation, and each exposure covered 0.3° in ω . The crystal to detector distance was 4.9 cm. Decay was monitored by repeating collection of the initial 50 frames collected and analyzing the duplicate reflections. Crystal decay was negligible. The space group was determined on the basis of systematic absences and intensity statistics.¹³ The structure was solved by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed in idealized positions with fixed isotropic displacement parameters equal to 1.5 times (1.2 for methyl protons) the equivalent isotropic displacement parameters of the atom to which they are attached.

The following programs were used: data collection and cell refinement, SMART;¹³ data reduction, SAINTPLUS (Bruker¹⁴); programs used to solve structures, SHELXS-97 (Sheldrick¹⁵); programs used to refine structures, SHELXL-99 (Sheldrick¹⁶); molecular graphics and publication materials, SHELXTL-Plus version 5.0 (Bruker¹⁷).

Results and Discussion

The model compound [hydrotris(3-phenylpyrazol-1-yl)borate]cadmium(II) acetate undergoes a rapid equilibrium between a five-coordinate and six-coordinate cadmium complex in the presence of an epoxide (eq 2). Utilizing a method developed by Popov, the equilibrium constant (K_{eq}) can be determined at various temperatures through a series of ^{113}Cd NMR experiments.¹⁸ A signal in the NMR spectra at ~ 155 ppm is typical of the five-coordinate species. Upon addition of 1 equiv of epoxide, the signal shifts upfield. The signal continues to shift upfield as the temperature is lowered and the equilibrium is shifted to the right. In the presence of a 10-fold excess of the respective epoxide, a signal at ~ 80 ppm is observed for all experiments at -80°C as the rapid equilibrium shifts to give a preponderance of the six-coordinate species.



(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Andres, J. L.; Gonzalez, A. C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2002.

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(13) SMART 1000 CCD; Bruker Analytical X-ray Systems: Madison, WI, 1999.

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

(15) Sheldrick, G. SHELXS-97, Program for Crystal Structure Solution; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1997.

(16) Sheldrick, G. SHELXL-99, Program for Crystal Structure Refinement; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1999.

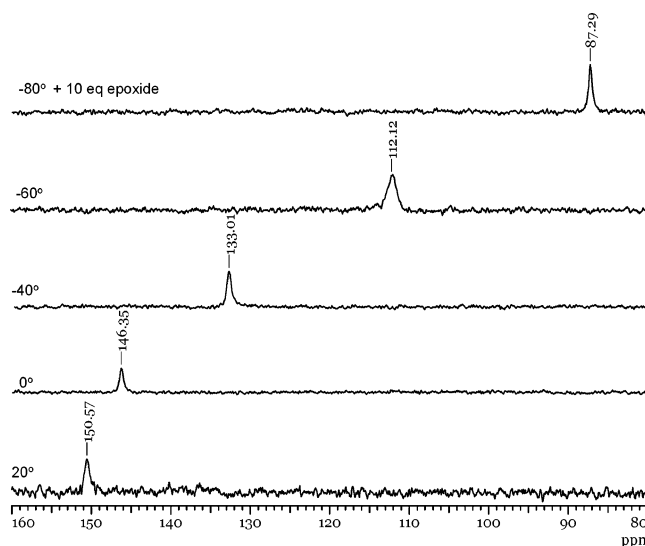


Figure 1. Temperature-dependent ^{113}Cd NMR spectra of $[\text{Tp}^{\text{Ph}}]\text{Cd}(\text{OAc}) + \text{B}$. Spectra from 20 to -60°C contain 1 equiv of epoxide. The spectrum at -80°C contains 10 equiv of epoxide.

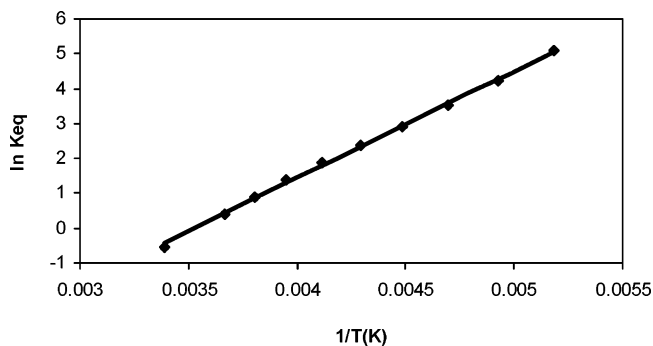


Figure 2. van't Hoff plot of K_{eq} at various temperatures for eq 2 determined from ^{113}Cd NMR spectra of $[\text{Tp}^{\text{Ph}}]\text{Cd}(\text{OAc}) + \text{B}$. Best fit line has $m = 3052.5$, $b = -10.761$, and $R^2 = 0.9988$.

Table 1. ^{113}Cd NMR Shifts for $[\text{Tp}^{\text{Ph}}]\text{Cd}(\text{OAc})$ in the Presence of Epoxides

substrate	^{113}Cd NMR shift at 20°C	^{113}Cd NMR shift at -80°C + 10-fold excess of epoxide
A	154	80
B	151	87
C	151	81
D	151	86
E	152	92
PPh_3	153	107

Table 1 gives the ^{113}Cd NMR shifts of $[\text{Tp}^{\text{Ph}}]\text{Cd}(\text{OAc})$ for the addition of each epoxide. The thermodynamic parameters for the binding of the epoxide substrate to the cadmium center are determined through van't Hoff plots as has been previously described for several cyclic ether substrates.⁶ A representative set of temperature-dependent ^{113}Cd NMR spectra for $[\text{Tp}^{\text{Ph}}]\text{Cd}(\text{OAc})$ in the presence of 1,4-dihydronaphthalene oxide (**B**) are provided in Figure 1. Figure 2 provides the van't Hoff plot. The thermodynamic parameters for the reaction in eq 2 and the previously examined $[\text{Cd}(\text{O}-2,6-\text{R}_2\text{C}_6\text{H}_3)_2]_2$ system defined in eq 3 for each epoxide are summarized

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

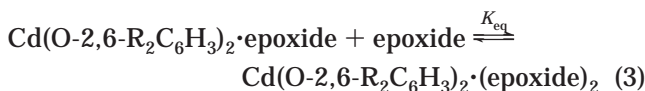
(18) Roach, E. T.; Hardy, P. R.; Popov, A. I. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 359.

Table 2. Thermodynamic Binding Parameters for [Tp^{Ph}]Cd(OAc) + Epoxide

substrate	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)	K_{298}
A	-38.70 ± 0.91	-138.70 ± 4.00	1.94 ± 1.2	0.217
B	-25.38 ± 0.20	-89.47 ± 0.84	1.28 ± 0.25	0.596
C	-26.70 ± 0.64	-92.09 ± 1.73	0.75 ± 0.52	0.740
D^a	-24.63 ± 0.55	-83.25 ± 2.38	0.18 ± 0.71	0.931
E	-22.13 ± 1.15	-78.82 ± 4.84	1.36 ± 1.40	0.578
PPh ₃	-31.40 ± 0.62	-109.96 ± 2.65	1.37 ± 0.79	0.576
CHO ^{6 b}	-24.7 ± 1.0	-95.4 ± 4.2	3.73 ± 1.00	0.222
PO ⁶	-24.3 ± 1.4	-94.1 ± 5.7	3.74 ± 1.35	0.221
THF ⁶	-27.7 ± 0.2	-89.7 ± 0.7	-1.00 ± 0.16	1.479

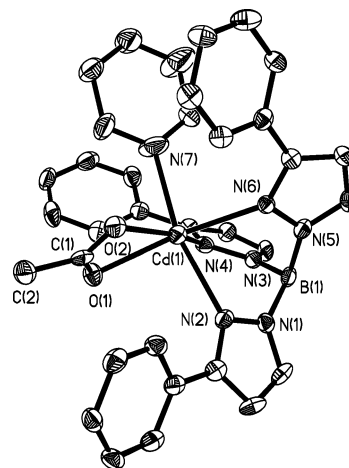
^a The corresponding data determined from reaction 3 are -33.9 ± 0.8, -112.0 ± 3.4, -0.49 ± 0.19, and 1.22. ^b The corresponding data determined from reaction 3 are -37.2 ± 1.5, -123.2 ± 6.4, -0.50 ± 0.37, and 1.23.

in Table 2. From these results it is apparent that there is very little variance among the values of ΔH° , with an average of -26.6 ± 2.4 kJ/mol. The greatest deviation from the average value of ΔH° is associated with binding to limonene oxide, which is 12.1 ± 2.6 kJ/mol higher than the average. It should however be noted that the thermodynamic binding parameters for **A** have the largest experimental errors. Despite the fact that the three-coordinate [Cd(O-2,6-R₂C₆H₃)₂]₂ system binds more strongly than the five-coordinate [Tp^{Ph}]Cd(OAc), there is little difference among the values for the representative examples in Table 2. Nevertheless, for comparative purposes it is best to have thermodynamic binding data for the various epoxides with a metal center containing a consistent ligand set.



As a comparison, the strongly donating ligands triphenylphosphine, trimethylphosphine, and piperidine were used in ¹¹³Cd NMR experiments similar to those involving the epoxides. The results for triphenylphosphine are listed in Table 2. Addition of trimethylphosphine to the cadmium complex results in the appearance of a signal at ~100 ppm at 20 °C that shifts slightly downfield as the temperature is lowered. The addition of piperidine to a CD₂Cl₂ solution of the cadmium complex results in the immediate formation of a precipitate. Both of these results indicate strong binding and immediate formation of the six-coordinate complex even at ambient temperature.

A structural investigation of the six-coordinate complex formed by each epoxide substrate, particularly a comparison of cadmium–epoxide bond lengths, would be desirable. Unfortunately, despite previous success at obtaining crystalline samples of the cyclohexene oxide (CHO) and propylene oxide (PO) adducts of [Tp^{Ph}]Cd(OAc),^{6,19} only the piperidine adduct was isolated in these studies (Figure 3). All attempts at isolating other epoxide adducts resulted in formation of the 2:1 complex, [Tp^{Ph}]₂Cd. The inability to obtain crystalline products for these particular derivatives results from the epoxides themselves being either solids or high-boiling ligands. A thermal ellipsoid plot of [Tp^{Ph}]₂Cd-

**Figure 3.** Thermal ellipsoid plot of [Tp^{Ph}]Cd(OAc)·piperidine shown at the 50% probability level. H atoms are omitted for clarity.**Table 3. Crystal Data and Structure Refinement for [Tp^{Ph}]Cd(OAc)·piperidine**

empirical formula	C ₃₄ H ₃₆ BCdN ₇ O ₂
fw	697.91
temp (K)	110(2)
cryst syst	monoclinic
space group	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	11.7368(17)
<i>b</i> (Å)	15.114(2)
<i>c</i> (Å)	18.074(3)
β (deg)	102.716(3)
<i>U</i> (Å ³)	3127.6(8)
<i>D</i> _c (Mg/m ³)	1.482
<i>Z</i>	4
μ (mm ⁻¹)	0.742
no. of reflns collected	13867
no. of indep reflns	4503
no. of params	407
goodness-of-fit on <i>F</i> ²	0.980
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ ^a = 0.0530 <i>wR</i> ₂ ^a = 0.1214

$$^a R = \sum |F_o| - |F_c| / \sum F_o \text{ and } R_{wF} = \{[\sum_w (F_o - F_c)^2] / \sum_w F_o^2\}^{1/2}.$$

(OAc)·piperidine is shown in Figure 3, and X-ray crystallography parameters are given in Table 3. As seen in other adducts, the structure displays distorted octahedral geometry with a chelating acetate ligand.^{6,19} Cadmium–acetate bond lengths (Cd(1)–O(1) and Cd(1)–O(2)) average 2.358 Å. The cadmium–piperidine bond length (Cd(1)–N(7)) is 2.348(5) Å. Bond angles that illustrate the octahedral distortion include N(6)–Cd(1)–O(1) (165.11(4)°), N(2)–Cd(1)–N(7) (166.3(2)°), and O(2)–Cd(1)–N(4) (158.64(16)°), which should be linear, as well as O(2)–Cd(1)–N(7) (85.12(17)°), which should be 90°.

In order to compare structural data with the results of the NMR experiments, we undertook DFT geometry optimizations of the epoxide adducts of [Tp^{Ph}]Cd(OAc) to determine the theoretical bond distances between the cadmium center and the various epoxides. First, we conducted computational studies on three known structures, [Tp^{Ph}]Cd(OAc)·CHO, [Tp^{Ph}]Cd(OAc)·PO, and [Tp^{Ph}]Cd(OAc)·THF.⁶ Table 4 compares key bond distances and angles between the DFT calculations and the previously determined crystal structures. The close agreement between the experimental and theoretical structures, especially in the case of the cadmium–cyclic ether bond length (Cd(1)–O(3)), encouraged us to pro-

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Table 4. Comparison of DFT and Crystal Structure Derived Geometric Parameters for Selected [Tp^{Ph}]Cd(OAc) Adducts

geometric value	[Tp ^{Ph}]Cd(OAc)·THF		[Tp ^{Ph}]Cd(OAc)·PO		[Tp ^{Ph}]Cd(OAc)·CHO	
	calcd	exptl	calcd	exptl	calcd	exptl
Cd(1)–O(3)	2.380 Å	2.388(8) Å	2.401 Å	2.414(4) Å	2.405 Å	2.395(4) Å
Cd(1)–N(2)	2.402 Å	2.397(9) Å	2.385 Å	2.380(4) Å	2.391 Å	2.384(5) Å
Cd(1)–N(4)	2.405 Å	2.323(9) Å	2.400 Å	2.312(4) Å	2.413 Å	2.325(4) Å
Cd(1)–N(6)	2.441 Å	2.321(8) Å	2.429 Å	2.321(4) Å	2.440 Å	2.331(4) Å
O(3)–Cd(1)–N(6)	165.5°	164.7(3)°	167.6°	164.46(14)°	166.8°	165.3(2)°
N(6)–Cd(1)–N(4)	84.3°	86.5(3)°	84.5°	86.35(12)°	82.8°	87.6(2)°

Table 5. DFT Cd–Epoxide Bond Distances for [Tp^{Ph}]Cd(OAc)·epoxide

epoxide	Cd–epoxide bond distance (Å)
A	2.409
B	2.403
C	2.427
D	2.416
E	2.448
cyclohexene oxide	2.405
propylene oxide	2.401

ceed with our calculations for the other substrates. Table 5 gives the calculated cadmium–epoxide bond distances. From Table 5 it can be observed that variances among these bond distances are minimal. In fact, little correlation can be made between the value of these bond distances and the thermodynamic parameters for reaction 2. Despite the fact that the Cd–epoxide bond distance is much larger in the cases of **C**, **D**, and **E**, there is very little difference in the values of ΔH° for reaction 2 for these epoxides and those of cyclohexene oxide, propylene oxide, and **B**. Indeed, the complex with the largest bond distance, that of Cd to α -pinene oxide (2.448 Å), has a ΔH° for reaction 2 nearly identical to that of the complex with the shortest bond distance (PO). The system with the most negative value of ΔH° , [Tp^{Ph}]Cd(OAc) + (+)-limonene oxide, has a theoretical bond distance for the epoxide adduct roughly equal to three of the other complexes. Figure 4 gives a plot of ΔH° vs Cd–O bond distances.

Conclusions

These experiments have given both a thermodynamic and structural comparison of the activation of epoxides through their ability to bind to a model catalyst complex, [Tp^{Ph}]Cd(OAc). The ¹¹³Cd NMR and computational experiments have shown that there is very little variation in the thermodynamic binding parameters or the structural bonding distances among the epoxides that easily ring-open (i.e., cyclohexene oxide, [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane) and those that do not (i.e., exo-norbornene oxide, 1,4-dihydronaphthalene oxide). A range of 0.217–0.931 is observed for K_{eq} . The theoretical Cd–epoxide bond distances range from 2.401

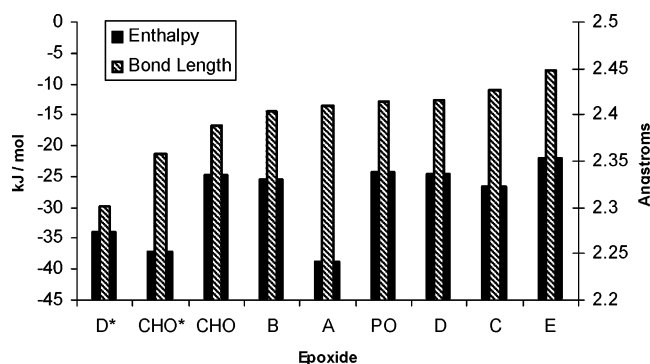


Figure 4. Bar graph of ΔH° vs Cd–O bond distance. Epoxides are listed in order of increasing bond lengths. Data relative to Cd(O-2,6-*tert*-butyl-C₆H₃)₂·epoxide (eq 3) are indicated by asterisk.^{4a}

to 2.448 Å. From these observations one can conclude that the ability of the epoxide to bind to a metal complex cannot be the only determining factor in its propensity to be ring-opened by a nucleophile, thus activating it toward copolymerization with CO₂. This conclusion is consistent with the proposed propagation step in the copolymerization of cyclohexene oxide and CO₂ in the presence of (salen)CrX catalysts, where kinetic measurements show the epoxide enchainment process to proceed without direct epoxide binding to the chromium center.²⁰

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Supporting Information Available: Complete details of the X-ray diffraction studies on [Tp^{Ph}]Cd(OAc)·piperidine. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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