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Syntheses and Structures of Epoxide Adducts of Soluble Cadmium(II) Carboxylates. Models for the Initiation Process in Epoxide/CO_2 Coupling Reactions

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Dicarboxylates of zinc(II) afford the most active catalysts to date for the copolymerization of CO_2 and epoxides to produce high molecular weight polycarbonates.[1,2] This polymerization process represents one of the few examples of an economically feasible catalytic incorporation of CO_2 into useful organic products.[3] Nevertheless, it is only marginally practical, suffering from such factors as low polymer yields and reproducibility, side reactions which afford cyclic carbonates, and the use of environmentally unfavorable solvents. This latter deficiency has been partially mitigated *via* the employment of supercritical carbon dioxide as both solvent and reactant.[4] More importantly, mechanistic investigations have been frustrated largely due to difficulties in assessing the nature of these heterogeneous catalysts.[5] Significant mechanistic studies are necessary in order to provide a better understanding of the intimate reactions involved in this process and, hence, improve its utility. This report describes the use of Cd(II) carboxylates, solubilized in organic solvents by the tris-3-phenylpyrazole hydroborate ligand,[6] as model reagents for the heterogeneous catalytic system. In particular the reactions of these carboxylate derivatives with epoxides to afford novel, isolable metal−epoxide complexes and their subsequent reactions to provide C−O bonds will be presented.

The ^{113}Cd nucleus being NMR active provides a highly sensitive spectroscopic probe for observation of its reaction chemistry.[7] Indeed, substitution of Zn(II) with Cd(II) has been used extensively to study zinc enzymes.[8] (η^3-HB(3-Phpz)$_3$)-Cd^{II}(acetate)·THF may be prepared by the addition of slightly less than 1 equiv of K[η^3-HB(3-Phpz)$_3$] to Cd(acetate)$_2$ in THF. Addition of H_2O results in the precipitation of product in high yields. One equivalent of THF per Cd ion was found in the resulting complex as verified by ^{1}H NMR and chemical analysis.[9] ^{113}Cd NMR indicated total dissociation of the THF adduct in chloroform or dichloromethane at room temperature as observed by a single resonance at 150 ppm relative to Cd(ClO$_4$)$_2$. The saturated six-coordinate species was observed at a resonance of 83.4 ppm at −90 °C in dichloromethane in the presence of excess THF.[10]

The observation of a labile THF at the Cd(II) center suggests the possibility of preparing a Cd(II) carboxylate complex with a coordinated epoxide ligand. Indeed, we have been able to isolate the corresponding propylene oxide and cyclohexene oxide derivatives (**1** and **2**, respectively) by a repeated dissolution of the THF complex in the epoxide solvent.[11] Because of the unusual nature of these complexes, we have characterized them by single-crystal X-ray diffraction.[12] The molecular structures of these complexes are depicted in Figures 1 and 2. Although the structure of a ruthenium(II) thiirane complex has been published,[13] only recently has the first crystal structure of a metal epoxide complex been reported for a ruthenium porphyrin derivative of styrene oxide.[14] One-to-one adducts of epoxides with Cd(II) porphyrins have been observed spectrophotometrically; however, to our knowledge the complexes presented herein represent the only other structurally characterized examples containing metal−epoxide binding.[15] In contrast to analogous Zn(II) carboxylates, which typically are four- or five-coordinate with unidentate or asymmetrically chelated carboxylate ligands,[16] these Cd(II) derivatives are six-coordinate with the acetate being rather symmetrically bonded to the metal

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(9) ^{1}H NMR for [η^3-HB(3-Phpz)$_3$]Cd(acetate)·THF: δ 1.73 [4H, br {THF}], 1.91 [3H, s, {Cd−O$_2$CC*H*$_3$}], 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}]. Anal. Calcd for $C_{33}H_{33}N_6O_3CdB$: C, 57.87; H, 4.86. Found: C, 57.26; H, 4.83.

(10) (a) Private communication with Professor D. Reger indicated that ^{113}Cd NMR resonances of similar N_3O_2Cd and N_3O_3Cd complexes are observed in these general regions. (b) Reger, D. L.; Mason, S. S.; Rheingold, A. L.; Ostrander, R. C. *Inorg. Chem.* **1993**, *32*, 5216.

(11) (a) ^{1}H NMR for [η^3-HB(3-Phpz)$_3$]Cd(acetate)·(propylene oxide): δ 1.30 [3H, d, {CH_3CHCH_2O}], 1.91 [3H, s, {Cd−O$_2$CC*H*$_3$}], 2.41 [1H, q, {CH$_3$C*H*CH$_2$O}], 2.75 [1H, t, {CH$_3$CHC*H*$_2$O}], 2.95 [1H, m, {CH$_3$CHC*H*$_2$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}]. Anal. Calcd for $C_{32}H_{31}N_6O_3CdB$: C, 57.29; H, 4.66. Found: C, 56.14; H, 4.69. (b) ^{1}H NMR for [η^3-HB(3-Phpz)$_3$]Cd(acetate)·(cyclohexene oxide): δ 1.1−1.5 [4H, m, {O(CH)$_2$(CH$_2$)$_2$(C*H*$_2$)$_2$}], 1.6−2.0 [7H, m, {O(CH$_2$)$_2$(CH$_2$)$_2$(C*H*)$_2$, CdO$_2$CC*H*$_3$}], 3.12 [2H, q, {O(C*H*$_2$)$_2$(CH)$_2$(CH$_2$)$_2$}], 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(3Ph*pz*)$_3$−Cd}]. Anal. Calcd for $C_{35}H_{35}N_6O_3CdB$: C, 58.80; H, 5.50. Found: C, 59.24; H, 5.43.

(12) The details of the structure analysis for compounds **1** and **2** may be found in the supplementary material. Complexes **1** and **2** were solved on a Siemens R3m/V X-ray diffractometer (oriented graphite monochromator; Mo Kα $\lambda = 0.710\,73$ Å radiation). Full-matrix least-square anisotropic refinement for all non-hydrogen atoms yielded $R_F = 4.17$, $R_{wF} = 9.22$, and $S = 1.06$ for **1** and $R_F = 4.87$, $R_{wF} = 11.29$, and $S = 1.0$ for **2**. Note: Both epoxide ligands were found to contain disordered atoms. In **1**, atoms C(3a) and C(5a) were refined with 45% partial occupancy and C(3b) and C(5b) were refined with 55% partial occupancy anisotropically. Atoms C(3b) and C(5b) in **1** were omitted for clarity. In **2**, atoms C(5), C(6), C(7), and C(8) were refined isotropically with 61% occupancy. Atoms C(5′), C(6′), C(7′), and C(8′) were refined isotropically with 39% partial occupancy. $R_F = \sum|F_o - F_o|/\sum F_o$. $R_{wF} = \{[\sum w(F_o^2 - F_o^2)^2]/[w(F_o^2)^2]\}^{1/2}$.

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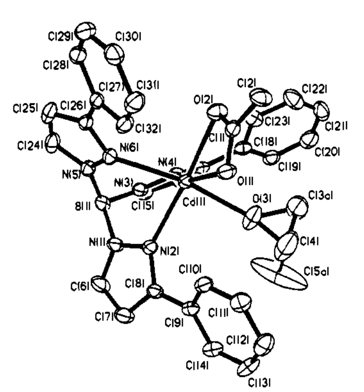


Figure 1. The molecular structure of the non-hydrogen atoms of 1. The thermal ellipsoids are drawn at the 30% probability level.

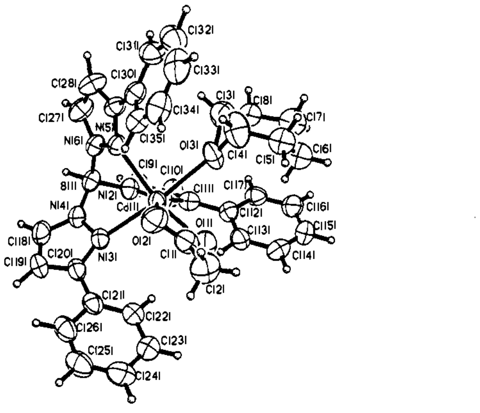


Figure 2. The molecular structure of the non-hydrogen atoms of 2. The thermal ellipsoids are drawn at the 50% probability level.

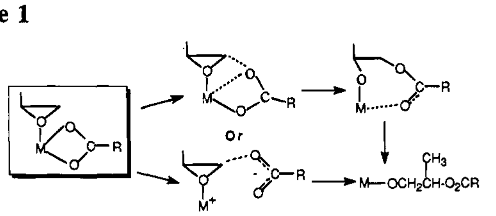
center. That is, the Cd–O(1) and Cd–O(2) bond distances are 2.300(4) and 2.346 Å, respectively, in 1 and 2.309 and 2.355 Å, respectively, in 2. The Cd–O distances for cyclohexene oxide (2.395(4) Å) and propylene oxide (2.414(4) Å) are similar, albeit the propylene oxide bond to Cd(II) is slightly weaker. The angle defined by the Cd–O vector and the midpoint of the OC_2 plane is about 140° in both derivatives.

At ambient temperature in methylene chloride, complexes 1 and 2 undergo complete epoxide dissociation to afford the corresponding five-coordinate complex (3) as indicated by a common ^{113}Cd resonance at 156 ppm (eq 1). On the other hand, at −90 °C in the presence of excess epoxide ligand, eq 1 shifts to the right to provide the six-coordinate complexes 1 and 2 with ^{113}Cd signals at 85.1 and 84.1 ppm, respectively. Initial competition studies utilizing equal molar mixtures of propylene oxide and cyclohexene oxide indicate only a slight preference for cyclohexene oxide binding to Cd(II) as compared with propylene oxide. However, it is clear from these studies, as well as others,[15] that there is thermodynamic selection for THF or propylene sulfide binding to the Cd(II) center when compared with either of these epoxides.[17]

$$\underset{\mathbf{3}}{(\eta^3\text{-HB(3-Phpz)}_3)\text{Cd(acetate)}} + \text{epoxide} \rightleftharpoons (\eta^3\text{-HB(3-Phpz)}_3)\text{Cd(acetate)}\cdot\text{epoxide} \quad (1)$$

These complexes represent the first isolated species which can be envisioned as intermediates in the initiation step for the

Scheme 1



polymerization of epoxides or the copolymerization of epoxide and carbon dioxide starting from metal carboxylates. Indeed, preliminary investigations illustrate carboxylate–epoxide coupling as outlined in Scheme 1, with subsequent processes affording homo-oligomers. That is, refluxing a cyclohexene oxide solution of the (η^3-HB(3-Phpz)$_3$)Cd^{II}(acetate)·THF adduct resulted in the formation of a homo-oligomerized product with an ester end group as seen by infrared and ^{1}H NMR spectroscopies.[18–20] This was verified by employing the 1-^{13}C, 99% labeled acetate derivative, (η^3-HB(3-Phpz)$_3$)Cd^{II}(acetate)·cyclohexene oxide.[21] When the analogous reaction with propylene oxide was carried out in the presence of CO_2 (1050 psi), in addition to the epoxide/carboxylate coupling reaction occurring, catalytically produced quantities of cyclic carbonate were also formed. Therefore, it is reasonable to expect that copolymerization of CO_2 and epoxides in the presence of complexes 1 or 2 may be possible under the appropriate set of reaction conditions. As indicated in Scheme 1 this epoxide–carboxylate coupling process may be occurring *via* a metal-bound or dissociated carboxylate ligand. Indeed, the kinetic lability of ligands associated with d^{10} metal ions suggests the involvement of an uncoordinated, more basic carboxylate group. However, these mechanistic details must await definitive kinetic studies, which are currently in progress.

In summary, complexes 1 and 2 represent well-characterized metal–epoxide complexes. Our studies indicate that the epoxide ligand is relatively weakly binding toward Cd(II), much more so than THF and thiirane ligands. Furthermore, we have observed coupling of the epoxide ligand with the carboxylate group in these metal complexes to subsequently provide oligomers of the epoxide with terminal ester groups. In analogous reactions carried out in the presence of carbon dioxide, cyclic carbonates are also formed. Hence, these cadmium complexes appear to be excellent models for mimicking the catalytic properties of the more reactive, poorly characterized catalysts derived from Zn(II) dicarboxylates.

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Supplementary Material Available: Tables giving a summary of crystal structure determination data, atomic coordinates, equivalent isotropic displacement coefficients, bond lengths and angles, and anisotropic thermal parameters for complexes 1 and 2 and ball-and-stick drawings of the molecular structures of complexes 1 and 2 along with atomic numbering schemes (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(18) IR (CH_2Cl_2): ν(CO) 1735 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.0–2.2 [br], 3.0–4.0 [br], 2.1 [s, {C*H*$_3$CO$_2$C}].[19]

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(20) In a typical run, M_n, the number average molecular weight, and M_w, the weight average molecular weight, were determined to be 286 and 1393, respectively, for the oligomers by GPC analysis.

(21) [η^3-HB(3-Phpz)$_3$]Cd(O$_2$^{13}CCH$_3$)·(cyclohexene oxide) was synthesized by the addition of labeled acetic acid to a cyclohexene oxide solution of the corresponding unlabeled complex. The ^{13}C resonance in the acetate complex at 179.7 ppm shifts to signals at 170.5 and 171.0 ppm for the ester group in the oligomer.