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Chromium(III) Octaethylporphyrinato Tetracarbonylcobaltate: A Highly Active, Selective, and Versatile Catalyst for Epoxide Carbonylation

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Abstract: The development of a highly active and selective porphyrin-based epoxide carbonylation catalyst, $[(OEP)Cr(THF)_2][Co(CO)_4]$ (**1**; OEP = octaethylporphyrinato; THF = tetrahydrofuran), is detailed. Complex **1** is a separated ion pair composed of a tetracarbonylcobaltate anion and an octahedral chromium porphyrin complex axially ligated by two THF ligands. Regarding the carbonylation of epoxides to β-lactones, catalyst **1** exhibits excellent turnover numbers (up to 10 000) and turnover frequencies (up to 1670 h^{-1}), with regioselective carbonyl insertion occurring between the oxygen and the sterically less hindered carbon of the epoxide substrate. Complex **1** is highly tolerant of nonprotic functional groups, carbonylating an array of aliphatic and cycloaliphatic epoxides, as well as epoxides with pendant ethers, esters, and amides. With careful control of reaction conditions in the carbonylation of glycidyl esters, the exclusive production of either the β- or γ-lactone isomer was achieved. Through analysis of reaction stereochemistry, a mechanism for the formation of γ-lactone products was proposed. Overall, a broad array of synthetically useful lactones has been synthesized in a rapid and selective fashion by catalytic carbonylation using $[(OEP)Cr(THF)_2][Co(CO)_4]$.

Introduction

The catalytic synthesis of β-lactones is of great interest due to the broad utility of these molecules in organic[2] and polymer chemistry,[3] as well as in natural product synthesis.[4,5] The energetically favored ring opening of four-membered lactones fuels a wide selection of subsequent reactions.[2] For example, nucleophilic attack at the carbonyl moiety results in cleavage of the acyl oxygen bond, which can then be trapped by an electrophile to attach two functional groups in one ring-opening reaction.[2] Reaction at the β-carbon of the lactone can be achieved using organometallic nucleophiles, providing for the synthesis of a range of carboxylic acids derived from carbon−oxygen bond scission.[6−8] Additional organic reaction pathways include syn-decarboxylation and enolate reactions.[2] The ring-opening polymerization of β-lactones by metal alkoxide catalysts gives high molecular weight poly(hydroxyalkanoate)s with narrow polydispersity.[9−14] These biodegradable polymers, which currently are produced through fermentation routes[15] and possibly in transgenic plants,[16] are targeted as substitutes for petroleum-derived materials.[3,17] The presence of the β-lactone moiety in numerous natural products and pharmaceuticals[4] demands the development of effective routes for its installation into complicated, highly functionalized molecules.

An attractive route to synthetically valuable β-lactones is the ring-expansive carbonylation of epoxides. The catalytic carbonylation of cyclic ethers has been studied for over half a century. Reppe first reported the carbonylation of tetrahydrofuran in the presence of water to give adipic acid.[18] Eisenmann et al., as well as Heck, reported the carboxymethylation of epoxides using cobalt catalysts in the presence of CO and alcohols.[19,20] Recent efforts in this field derive from the milestone achievements

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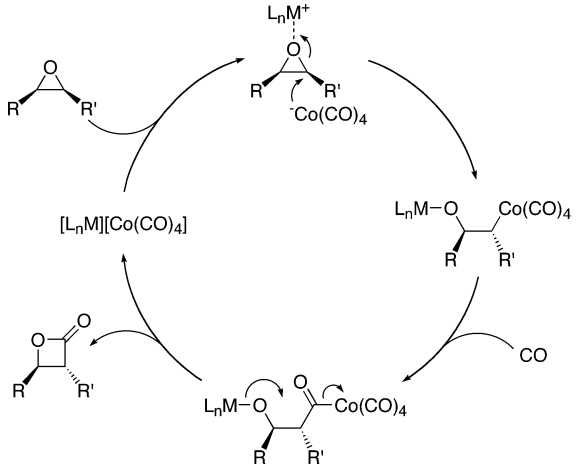
reported by Drent and Kragtwijk in 1994, involving the use of $Co_2(CO)_8$ and 3-hydroxypyridine to effect the carbonylation of epoxides to form β-lactones and polyester oligomers[21] under high pressures of carbon monoxide.[22,23] Alper and co-workers have shown that by the combination of $BF_3{\cdot}OEt_2$, a neutral Lewis acid, with $[PPN][Co(CO)_4]$ (PPN = $Ph_3P{=}N^+{=}PPh_3$) in dimethoxyethane, substantial rate enhancements could be achieved.[24] Alper applied this system to the carbonylation of a number of simple epoxides, providing the first demonstration of the versatility of this reaction. More recently, contributions from Rieger and co-workers have focused on empirical and theoretical studies employing a number of simple Lewis acids, with experimental observations limited to the carbonylation of propylene oxide.[25−27] Exploration of the energies of the ground- and transition-state structures using density functional theory (DFT) has helped to confirm the mechanism of epoxide carbonylation.[26] In the last three years, we have developed well-defined catalysts of the form [Lewis acid][$Co(CO)_4$] for the carbonylation of epoxides and aziridines with high activity and excellent selectivity.[28−31] Recently, we reported the porphyrin-based catalyst $[(TPP)Cr(THF)_2][Co(CO)_4]$ (TPP = tetraphenylporphyrinato), a highly active and selective epoxide carbonylation catalyst that was also effective for the carbonylation of cycloaliphatic epoxides.[30]

The hydrolytic kinetic resolution of epoxides, as developed by Jacobsen and co-workers, has provided a facile route to enantiomerically pure epoxides with side chains containing halogen, ether, ester, ketone, carbamate, aryl, vinyl, and alkynyl groups.[32−35] The availability of chiral-functionalized epoxides (and their corresponding diols) has led to shorter and more efficient syntheses of various natural products.[36−40] Subsequent catalytic reactions of epoxides that preserve chirality are highly valued in these continued synthetic efforts. In previous reports, we have shown that [Lewis acid][$Co(CO)_4$] complexes catalyze the carbonylation of epoxides and aziridines to form β-lactones and β-lactams in a stereospecific fashion (Scheme 1).[28−31] Herein, we present a new chromium(III) porphyrin-derived carbonylation catalyst that displays activities significantly higher than those reported in all previous studies, while maintaining the high yields and purity that have characterized this class of [Lewis acid][$Co(CO)_4$] catalysts. In addition, a comprehensive study exploring the range of epoxides amenable to this carbonylation reaction is reported. As such, epoxides with ether, ester, and amide functionality can now be carbonylated rapidly and selectively, as detailed below.

Scheme 1. Postulated Mechanism of Epoxide Carbonylation Using $[L_nM][Co(CO)_4]$ Catalysts



Results and Discussion

Catalyst Synthesis. The porphyrin-based catalyst $[(OEP)Cr(THF)_2][Co(CO)_4]$ (**1**; OEP = octaethylporphyrinato; THF = tetrahydrofuran; Figure 1) was generated by the metathesis of $NaCo(CO)_4$ with (OEP)CrCl. The byproduct NaCl was removed by filtration, and **1** was isolated as a red crystalline solid. This paramagnetic complex has a magnetic susceptibility of 3.70 μ_B, indicating that three unpaired electrons are present at the chromium center.[41] IR spectroscopy reveals a strong band at 1885 cm^{-1} for the $[Co(CO)_4^-]$ anion, as observed in various related compounds.[30,42,43] Additionally, the crystalline $[(OEP)Cr(THF)_2][Co(CO)_4]$ is quite robust, showing no decomposition at temperatures as high as 250 °C.

Solid-State Structure of 1. X-ray quality crystals of **1** were obtained by slow diffusion of pentane into a saturated THF solution.[44] The solid-state structure of **1** reveals a well-separated ion pair (Figure 2).[45] In the cationic unit, a tetradentate porphyrinato ligand and two molecules of axially coordinated THF provide for pseudo-octahedral coordination to the chro-

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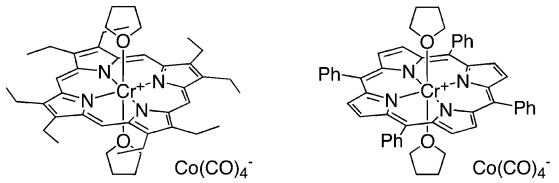

[(OEP)Cr(THF)$_2$][Co(CO)$_4$]; **1** [(TPP)Cr(THF)$_2$][Co(CO)$_4$]; **2**

Figure 1. Cr(III) porphyrin-based epoxide carbonylation catalysts.

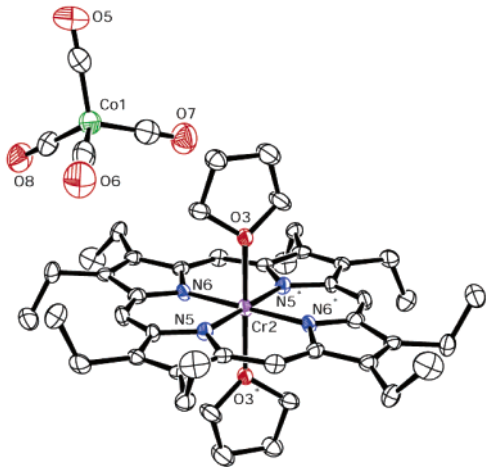

Figure 2. ORTEP view of **1** drawn with 50% thermal ellipsoids.

mium center. The anionic unit is comprised of tetrahedral $[Co(CO)_4]^-$. The bond lengths and angles at the chromium center are similar to those observed in other chromium porphyrin complexes.[46−51] The $[Co(CO)_4]^-$ anion is structurally the same as that found in related structures[52−55] and shows no covalent interactions with the chromium center (Co−Cr distance = 6.52 Å).

Epoxide Carbonylation. Catalyst **1** was initially screened for epoxide carbonylation activity with the substrate/catalyst loadings that proved optimal for the related catalyst, [(TPP)-Cr(THF)$_2$][Co(CO)$_4$] (**2**, Figure 1).[30] While retaining the high selectivity observed in our previous systems,[28−30] catalyst **1** exhibited substantially increased carbonylation activity. For most substrates, **1** was more than an order of magnitude faster than had been observed with **2**, the catalyst we previously reported to be the most active and selective.[30] At the current time, the origin of this difference is not clear, but we suspect the higher solubility and more electron-releasing ligand of **1** are responsible, in part, for the increased activity. Following the initial screening, substrate/catalyst loadings were optimized for catalyst **1**, generating >99% yield of lactone for a range of epoxides. All activities were determined by employing the standard conditions developed in our laboratory: neat substrate, CO (900 psi), 60 °C, and 6 h. Since optimized reactions reached completion at the end of the 6 h run, qualitative rate data could be obtained from the optimized substrate/catalyst loadings, assuming the absence of trace impurities that might impede reactions at low catalyst loadings. Once optimized, the scope of **1** was investigated by applying it to the carbonylation of numerous epoxides with subsidiary functionality tethered to the oxirane ring. The observed functional group tolerance of **1** further demonstrates the potential utility of this catalyst in organic, polymer, and natural product synthesis.

Optimized substrate/catalyst loadings for the carbonylation of simple hydrocarbon-based epoxides with **1** are listed in Table 1. The observed catalytic activities of **1** for the carbonylation of 1,2-epoxyalkanes (C_4−C_{12}) greatly surpass all previously reported catalysts, with turnover frequencies (TOFs) as high as 1670 h^{-1} (Table 1, entries 1−4). Interestingly, reactivity rates parallel chain length for these epoxides, with longer side chains resulting in faster carbonylation. Since the electronic properties vary only slightly in these substrates, we attribute this trend to solvent polarity effects, as these reactions are carried out in neat substrate. Sterically bulky epoxides can also be carbonylated effectively by **1**, as evidenced by the rapid carbonylation of *tert*-butyloxirane (**11**, entry 5). The use of unsaturated epoxides, such as 1,2-epoxy-5-hexene (**13**), impacts the carbonylation reaction minimally (entry 6). A comparison of saturated and unsaturated epoxides derived from the same carbon framework (entries 2 and 6) reveals only a slight reduction in reaction rate for the alkene. Importantly, the pendant alkene does not appear to insert into the postulated Co alkyl or acyl species (Scheme 1). Finally, internal epoxides can be carbonylated, as demonstrated with *trans*-2,3-epoxybutane (**15**, entry 7). To prevent product oligomerization, it was necessary to dilute this epoxide slightly (25 wt % added toluene). The formation of the *cis*-lactone (**16**) from *trans*-2,3-epoxybutane (**15**) with catalyst **1** is consistent with our previous studies of [Lewis acid][Co(CO)$_4$] catalysts, suggesting a similar mechanism (Scheme 1).[28−31] Applying standard reaction conditions to *cis*-2,3-epoxybutane resulted in rapid oligomerization, limiting lactone formation. Overall, a 6- to 22-fold increase in reactivity rate was observed when comparing **1** with the previously reported **2**.[30]

A wide selection of glycidyl ethers can be successfully carbonylated, yielding substituted hydroxymethyl lactone derivatives, as shown in Table 2. The carbonylation of alkyl glycidyl ethers exhibited faster reactivity with increased alkyl chain length, as was observed with the 1,2-epoxyalkanes (Table 2, entries 1 and 2). A glycidyl silyl ether was also carbonylated with high activity (Table 2, entry 3), while ethers containing unsaturated groups (benzyl, furfuryl, and allyl) reacted with moderate activities (entries 4−6). In the case of allyl glycidyl ether (**27**), the product lactone (**28**), a viscous oil, necessitated the addition of solvent (25 wt % toluene) to reach high conversion. The yield of **28** was limited to ∼55% when carried out with neat epoxide. Comparing the activities of catalysts **1** and **2** for the carbonylation of glycidyl ethers showed an increase in reactivity rate of 12-fold (entry 2) and 4-fold (entry 3), respectively.[30] The overall tolerance of catalyst **1** to a wide array of glycidyl ethers allows for the synthesis of protected and functionalized hydroxymethyl-β-propiolactone derivatives.

The catalytic carbonylation of cycloaliphatic epoxides was first achieved for 8- and 12-membered hydrocarbon rings in

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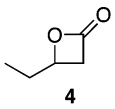
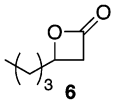
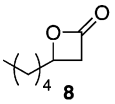
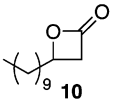
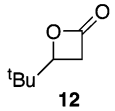
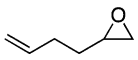
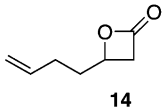
Table 1. Carbonylation of Aliphatic Epoxides Using [(OEP)Cr(THF)$_2$][Co(CO)$_4$] (**1**)[a]

entry	substrate	substrate/**1**	product	yield[b]
1	 **3**	3500	 **4**	> 99%
2	 **5**	4500	 **6**	> 99%
3	 **7**	5000	 **8**	> 99%
4	 **9**	10000	 **10**	> 99%
5	 **11**	5000	 **12**	> 99%
6	 **13**	3500	 **14**	> 99%
7[c]	 **15**	450	 **16**	88%

[a] Conditions: neat epoxide, 60 °C, 6 h, 900 psi CO. [b] Determined by ^{1}H NMR spectroscopy. [c] With 25 wt % toluene added.

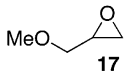
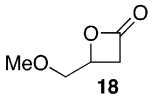
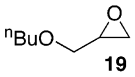
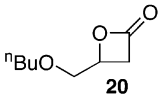
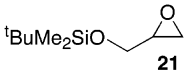
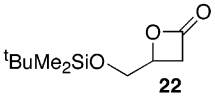
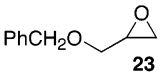
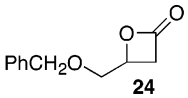
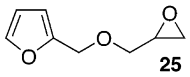
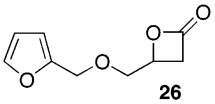
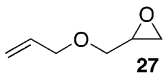
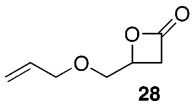
our previous report employing catalyst **2**.[30] The optimized substrate/catalyst ratios for carbonylation of these epoxides using catalyst **1** are presented in Table 3. Though previously uninvestigated with **2**, cyclopentene oxide (**29**) was found to carbonylate slowly (100 equiv in 24 h) to form the *cis*-lactone product (**30**, Table 3, entry 1).[56] This was unexpected, as the generally accepted mechanism for carbonylation with [Lewis acid][Co(CO)$_4$] systems predicts the formation of the *trans*-lactone product due to an S_N2 attack of the activated epoxide by [Co(CO)$_4$]$^-$ (Scheme 1). We calculated a difference of about 45 kcal/mol between the isomeric *cis*- and *trans*-lactone products (AM1 level: −18.7 kcal/mol (*trans*) vs −63.2 kcal/mol (*cis*)).[57] The high relative energy of the *trans* isomer helps to explain why only the *cis*-lactone product was generated under our reaction conditions. We propose that the carbonylation of cyclopentene oxide proceeds via a cationic mechanism (Scheme 2), allowing access to the *cis*-lactone product that cannot be produced with an S_N2 mechanism. In this modified mechanism, coordination of the Lewis acid to the epoxide results in the formation of a ring-opened, secondary carbocation. Trapping of the cation by [Co(CO)$_4$]$^-$ yields a cobalt alkyl complex with *cis* stereochemistry that can insert CO and ring-close to form *cis*-lactone (**30**). We have tentatively discounted the presence of β-H isomerization mechanisms due to the absence of cyclopentenol or cyclopentanone byproducts.

Larger cycloaliphatic epoxides were carbonylated in the usual manner, with *cis*-epoxides forming *trans*-lactones and vice versa. The reaction rates for cyclooctene derivatives with catalyst **1** were comparable to those obtained with catalyst **2** (Table 3, entries 2 and 3).[30] Both cyclooctene oxide (**31**) and 1,5-cyclooctadiene monoepoxide (**33**) were carbonylated to form exclusively *trans*-lactones. The larger cyclododecane rings, however, showed a modest rate enhancement when using catalyst **1** (entries 4 and 5). In the case of cyclododecene oxide (66% *cis*, **35**), carbonylation of the *cis*-epoxide is favored, allowing for the formation of almost exclusively *trans*-lactone (**36**, Table 3, entry 4). Additionally, *trans*-1,2-epoxy-*trans*-5-*trans*-9-cyclododecadiene (**37**) was carbonylated to the *cis*-lactone (**38**), albeit slowly (Table 3, entry 5).

The superior activities observed with **1** led us to investigate its substrate functionality tolerance, with a focus on the carbonylation of epoxides containing stronger Lewis basic side chains, such as esters, amides, and carbonates. To our surprise, carbonylation of glycidyl esters (**39**, **41**, and **43**) under standard reaction conditions (60 °C, 6 h) yielded a mixture of isomeric β- and γ-lactones. We postulated that the β-isomer was formed initially, as depicted in Scheme 1, followed by a slow isomerization to the γ-lactone. Reduction of the substrate/catalyst ratio for the carbonylation of these esters produced more γ-lactone, supporting this assertion. Lowering the reaction temperature to 40 °C resulted in the exclusive formation of the desired β-lactones. Optimized reaction conditions for the carbonylation of glycidyl acetate (**39**), butyrate (**41**), and benzoate (**43**) to form

(56) Vaughan, W. R.; Cartwright, W. F.; Henzi, B. *J. Am. Chem. Soc.* **1972**, *94*, 4978−4984.
(57) *Spartan '02*, version 1.0.4; Wavefunction, Inc.: Irvine, CA.

Table 2. Carbonylation of Glycidyl Ethers Using $[(OEP)Cr(THF)_2][Co(CO)_4]$ (**1**)[a]

entry	substrate	substrate/**1**	product	yield[b]
1	 **17**	750	 **18**	> 99%
2	 **19**	2500	 **20**	> 99%
3	 **21**	1800	 **22**	> 99%
4	 **23**	1000	 **24**	> 99%
5	 **25**	250	 **26**	> 99%
6[c]	 **27**	250	 **28**	88%

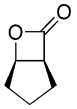
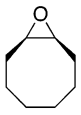
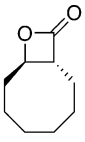
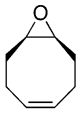
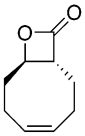
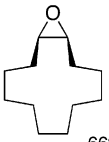
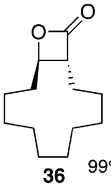
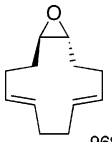
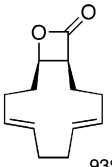
[a] Conditions: neat epoxide, 60 °C, 6 h, 900 psi CO. [b] Determined by ^{1}H NMR spectroscopy. [c] With 25 wt % toluene added.

the corresponding β-lactones are given in Table 4 (entries 1−3). These products were readily isolated by column chromatography (silica gel, $CHCl_3$) without degradation. Using (*R*)-glycidyl butyrate ((*R*)-**41**), the corresponding chiral β-lactone ((*R*)-β-(butyroxymethyl)-β-propiolactone; (*R*)-**42**) was also prepared. In a control experiment, β-(butyroxymethyl)-β-propiolactone (**42**) was found to isomerize readily to the γ-lactone (**46**) using $MgBr_2$ as a Lewis acid catalyst. The corresponding γ-lactones were obtained in high yields by extending reaction times to 24 h at the normal reaction temperature of 60 °C (Table 4, entries 4−6). This demonstrates that, for glycidyl esters, epoxide carbonylation and Lewis acid-catalyzed ring expansion can be coupled in one-pot syntheses of β-hydroxy-γ-butyrolactone esters without the formation of undesirable side products. This constitutes an effective new route to the formation of γ-butyrolactone derivatives, potentially useful in the synthesis of pharmaceuticals and natural products based on this framework.[58−60]

The ring expansion of β-lactones to yield γ-lactones has been observed previously with magnesium halides as Lewis acid catalysts.[61−65] Two related mechanisms have been proposed. The first involves a dyotropic (concerted) ring expansion,[62−65] while the second invokes a transient, zwitterionic species coupled to rapid stepwise migration.[61] A reasonable mechanism for the formation of γ-lactones from the ester-functionalized β-lactones using **1** is shown in Scheme 3. In the first step, coordination of the lactone carbonyl to the Lewis acid activates the β-carbon, increasing its susceptibility to attack by the carbonyl oxygen of the ester side chain (Scheme 3, **A**). This forms a resonance-stabilized carbocation within a 1,3-dioxolane framework (Scheme 3, **B**).[66,67] Reopening of the dioxolane ring to restore the ester side chain proceeds through carboxylate attack at the methylene to give the observed ring-expanded product. The net result of these two steps is a ring-expansive isomerization with inversion of stereochemistry at the stereogenic carbon of the reactant β-lactone. To provide experimental evidence for this mechanism, (*R*)-glycidyl butyrate ((*R*)-**41**) was carbonylated to form the γ-lactone. As noted above, carbonylation initially proceeds to form the β-lactone with retention of configuration at the chiral center, yielding (*R*)-β-butyroxymethyl-β-propiolactone ((*R*)-**42**). Subsequent isomerization of (*R*)-**42** yielded (*S*)-β-butyroxy-γ-butyrolactone ((*S*)-**46**), consistent with the mechanism detailed in Scheme 3. This product was confirmed by comparison of its optical rotation with a

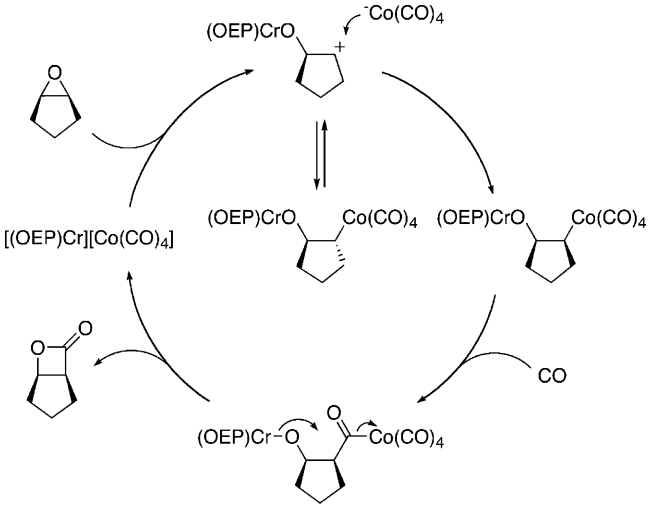
(58) Brown, S. P.; Bal, B. S.; Pinnick, H. W. *Tetrahedron Lett.* **1981**, *22*, 4891−4894.
(59) Ikan, R.; Weinstein, V.; Ravid, U. *Org. Prep. Proced. Int.* **1981**, *13*, 59−70.
(60) Koch, S. S. C.; Chamberlin, A. R. *Stud. Nat. Prod. Chem.* **1995**, *16*, 687−725.
(61) Metzger, C.; Borrmann, D.; Wegler, R. *Chem. Ber.* **1967**, *100*, 1817−1823.
(62) Mulzer, J.; Bruntrup, G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 793−794.
(63) Black, T. H.; Fields, J. D. *Synth. Commun.* **1988**, *18*, 125−130.
(64) Thompson, K. L.; Chang, M. N.; Chiang, Y. C. P.; Yang, S. S.; Chabala, J. C.; Arison, B. H.; Greenspan, M. D.; Hanf, D. P.; Yudkovitz, J. *Tetrahedron Lett.* **1991**, *32*, 3337−3340.
(65) Reetz, M. T.; Schmitz, A.; Holdgrun, X. *Tetrahedron Lett.* **1989**, *30*, 5421−5424.
(66) Winstein, S.; Buckles, R. E. *J. Am. Chem. Soc.* **1942**, *64*, 2780−2786.
(67) Pigman, W.; Horton, D., Eds. *The Carbohydrates: Chemistry and Biochemistry*; 2nd ed.; Academic Press: New York, 1972; Vol. 1A.

Table 3. Carbonylation of Alicyclic Epoxides Using [(OEP)Cr(THF)$_2$][Co(CO)$_4$] (**1**)[a]

entry	substrate	substrate/**1**	product	yield[b]
1[c]	 **29**	100	 **30**	> 99%
2	 **31**	250	 **32**	> 99%
3	 **33**	100	 **34**	> 99%
4	 **35** 66% *cis*	600	 **36** 99% *trans*	66%
5	 **37** 96% *trans*	100	 **38** 93% *cis*	57%

[a] Conditions: neat epoxide, 60 °C, 6 h, 900 psi CO. [b] Determined by ^{1}H NMR spectroscopy. [c] Reaction time: 24 h.

Scheme 2. Proposed Mechanism for Cyclopentene Oxide Carbonylation Using **1**

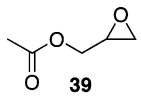
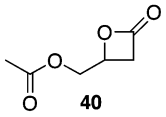
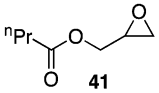
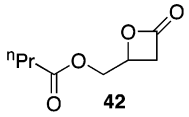
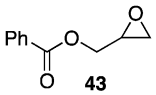
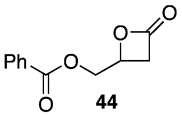
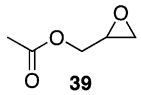
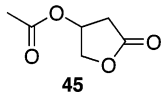
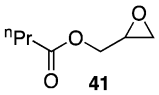
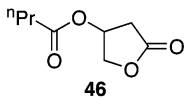
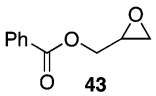
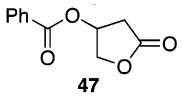
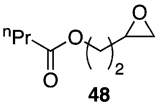
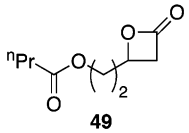
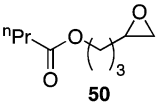
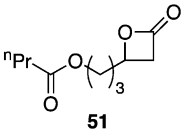
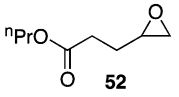
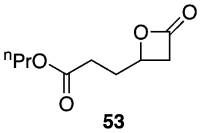
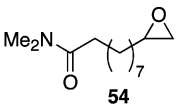
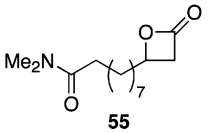


sample of known configuration, synthesized by the reaction of (*S*)-β-hydroxy-γ-butyrolactone with butyryl chloride.

Epoxides with butyryl groups attached through 2- and 3-carbon linkers (**48**, **50**) were synthesized and found to carbonylate rapidly to the corresponding β-lactones (Table 4, entries 7 and 8). The observed activities were on the order of those for 1,2-epoxyalkanes, indicating that the pendant esters caused little or no inhibition of the carbonylation reaction. The lack of γ-lactone formation for these substrates is most likely a result of the inaccessibility of the larger carbocationic rings necessitated by the proposed isomerization mechanism. Additional support for the ring-expansion mechanism illustrated in Scheme 3 is provided by the carbonylation of propyl 4,5-epoxypentanoate (**52**, Table 4, entry 9). Although this substrate is isomeric with the two-carbon-linked epoxide (**48**), a substantial reduction in rate was observed (see Table 4, entries 7 and 9). This can be attributed to the formation of a cyclic carbocation that has no available isomerization pathway. Instead, the carbocation is forced to revert to the β-lactone product (**53**), amounting to a net increase in coordination to the Lewis acid catalyst with no further reactivity.

Epoxides with pendant amides and carbonates were also probed as substrates for carbonylation. When functionalized with a long-chain amide (Table 4, entry 10), the epoxide reactivity rate was substantially reduced (TOF = 12 h^{-1}). The amide-tethered β-lactone, however, was still produced in quantitative yield. Reversible coordination of the amide to [(OEP)Cr]$^+$ is likely the cause of the severe inhibition observed. Carbonylation of allyl glycidyl carbonate (**56**) proved unsuccessful, yielding only an allyloxymethyl-substituted cyclic carbonate (**57**) as a result of a Lewis acid-mediated isomerization (Scheme 4). This product was identified spectroscopically by comparison with

Table 4. Carbonylation of Glycidyl Carboxylates Using [(OEP)Cr(THF)$_2$][Co(CO)$_4$] (**1**)[a]

entry	substrate	substrate/**1**	conditions	product	yield[b]
1	 **39**	300	40 °C, 6 h	 **40**	> 99%
2	 **41**	450	40 °C, 6 h	 **42**	> 99%
3	 **43**	250	40 °C, 6 h	 **44**	97%
4	 **39**	550	60 °C, 24 h	 **45**	> 99%
5	 **41**	300	60 °C, 24 h	 **46**	> 99%
6	 **43**	250	60 °C, 24 h	 **47**	> 99%
7	 **48**	3500	60 °C, 6 h	 **49**	> 99%
8	 **50**	3500	60 °C, 6 h	 **51**	> 99%
9	 **52**	1500	60 °C, 6 h	 **53**	> 99%
10	 **54**	75	60 °C, 6 h	 **55**	> 99%

[a] Conditions: neat epoxide, 900 psi CO. [b] Determined by ^{1}H NMR spectroscopy.

previous reports[68] and was produced in quantitative yield with a moderate rate (TOF = 60 h^{-1}).

Effect of CO Pressure. Although epoxide carbonylation by catalyst **1** proceeded rapidly with high selectivity, a moderate pressure dependence was observed. Reduction of the CO pressure to 200 psi resulted in little or no loss in catalyst activity for most substrates, as evidenced by the carbonylation of glycidyl *tert*-butyldimethylsilyl ether (**21**) with 98% conversion to the corresponding lactone (**22**) (epoxide/catalyst = 1800, CO (200 psi), 60 °C, 6 h). Further reduction of the CO pressure to 100 psi resulted in a substantial drop-off in activity, although the corresponding lactones still comprised the primary products in these reactions. In contrast to the reactions at higher pressure, small amounts (~5%) of the isomeric (noncarbonylated) ketones were observed. Product lactones were isolated cleanly via distillation, easily removing this byproduct. Although somewhat

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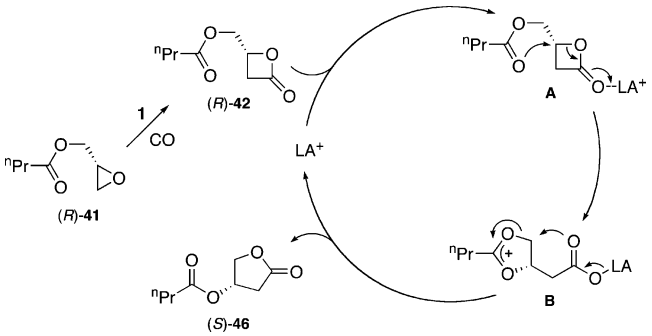
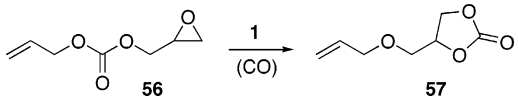
Scheme 3. Proposed Mechanism for Ring-Expansion of Ester-Functionalized β-Lactones



Scheme 4. Isomerization of Allyl Glycidyl Carbonate with **1**



slower, the general success of epoxide carbonylation at lower pressures provides access to functionalized lactones in any general synthetic laboratory.

Conclusions

We have demonstrated the synthesis and utility of a new carbonylation catalyst, $[(OEP)Cr(THF)_2][Co(CO)_4]$ (**1**). For most substrates, carbonylation rates using this catalyst were more than an order of magnitude faster than previously reported catalysts. The range of epoxides amenable to this reaction pathway has been expanded to include those containing ester and amide side chains. Due to this broad applicability, **1** is an ideal catalyst for the carbonylation of epoxides, with possible applications ranging from bulk organic syntheses to pharmaceutical and fine-chemical production. The unprecedented turnover frequencies of **1** allow for minimal catalyst loadings, simplifying product isolation and removal of trace metals. Overall, the high activities and broad substrate tolerance of **1** mark it as a highly versatile epoxide carbonylation catalyst. Future work will focus on the conclusive determination of the mechanism operable in these systems and the development of new catalysts for enantioselective epoxide carbonylation.

Experimental Section

General Considerations. Standard Schlenk line and glovebox techniques were used in the synthesis and reactions of catalyst **1**. All organic reactions were carried out under ambient atmosphere. The product lactones are air stable and can be handled under ambient atmosphere. Pentane and tetrahydrofuran (THF) were purified by passage through commercial solvent purification columns and degassed prior to use. (OEP)CrCl was purchased from Mid-Century Chemicals and used as received. 1,2-Epoxybutane (**3**), 1,2-epoxyhexane (**5**), 1,2-epoxydodecane (**9**), 1,2-epoxy-5-hexene (**13**), *trans*-2,3-epoxybutane (**15**), glycidyl methyl ether (**17**), glycidyl *n*-butyl ether (**19**), glycidyl *tert*-butyldimethylsilyl ether (**21**), benzyl glycidyl ether (**23**), furfuryl glycidyl ether (**25**), cyclopentene oxide (**29**), cyclooctene oxide (**31**), 1,5-cyclooctadiene monoepoxide (**33**), cyclododecene oxide (66% *cis*, **35**), (*R*)-glycidyl butyrate ((*R*)-**41**), 3-buten-1-ol, 4-penten-1-ol, triethylamine, butyryl chloride, 4-pentenoyl chloride, *m*-chloroperoxybenzoic acid, and (*S*)-β-hydroxy-γ-butyrolactone were purchased from Aldrich. 1,2-Epoxy-*trans*-5-*trans*-9-cyclododecadiene (96% *trans*, **37**) was purchased from Lancaster. Allyl glycidyl ether (**27**) was purchased from TCI America. 1,2-Epoxyheptane (**7**),[69] *tert*-butyl oxirane (**11**),[70] glycidyl acetate (**39**),[71] glycidyl butyrate (**41**),[71] glycidyl benzoate (**43**),[72] *N*,*N*-dimethyl-10,11-epoxyundecylamide (**54**),[73] allyl glycidyl carbonate (**56**),[74] and $NaCo(CO)_4$[75] were synthesized as previously reported. Full characterization of the remaining epoxides can be found below. All liquid epoxides were dried over CaH_2 and vacuum distilled prior to use; solids were used as received. Carbon monoxide was purchased from Matheson and used without further purification. NMR chemical shifts are given relative to residual $CHCl_3$ (^{1}H δ 7.26) and $CDCl_3$ (^{13}C δ 77.23). The ^{1}H NMR spectra of product lactones were identified by comparison with published spectra for β-valerolactone (**4**),[76] β-heptanolactone (**6**),[77] β-octanolactone (**8**),[78] β-tridecalactone (**10**),[77] 4-*tert*-butyl-2-propiolactone (**12**),[79] 4-(but-3-enyl)-2-propiolactone (**14**),[24] *cis*-3,4-dimethyl-2-propiolactone (**16**),[28] 4-(butyloxymethyl)-2-propiolactone (**20**),[30] 4-(*tert*-butyldimethylsiloxymethyl)-2-propiolactone (**22**),[30] 4-(benzyloxymethyl)-2-propiolactone (**24**),[80] *cis*-6-oxabicyclo[3.2.0]heptan-7-one (**30**),[56] *trans*-9-oxabicyclo[6.2.0]decan-10-one (**32**),[81] *trans*-9-oxabicyclo[6.2.0]dec-4-en-10-one (**34**),[82] *trans*-13-oxabicyclo[10.2.0]tetradecan-14-one (**36**),[30] *cis*,*trans*-13-oxabicyclo[10.2.0]tetradeca-*trans*-4-*trans*-8-dien-14-one (**38**),[30] and β-acetoxy-γ-butyrolactone (**45**).[83] ^{1}H and ^{13}C NMR spectra for the remaining lactones are given below. Melting points were acquired in sealed capillary tubes under nitrogen and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 digital polarimeter with a sodium lamp and are reported with format: $[\alpha]^T_D\, r$ (*c*, solvent), where T = temperature in °C, D refers to the sodium D line (589 nm), r is the measured rotation, and c is the concentration in g/100 mL. IR spectra were measured on a Mattson Research Series FTIR. High-resolution mass spectra were obtained from the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, employing electron impact conditions. Magnetic susceptibility was measured in THF-d_8 using Evans' NMR method.[84] Elemental analyses were carried out by Desert Analytics in Tucson, Arizona.

$[(OEP)Cr(THF)_2][Co(CO)_4]$ (1). Under an atmosphere of nitrogen, a solution of $NaCo(CO)_4$ (160 mg, 0.820 mmol) in THF (20 mL) was added to a flask containing (OEP)CrCl (498 mg, 0.803 mmol) and THF (20 mL). The dark-red solution was stirred for 24 h and then allowed to stand and settle. The resulting material was filtered, and the residual solid was washed with several portions of THF (totaling 40 mL) to maximize product recovery. After concentrating to 20 mL in vacuo, the solution was layered with pentane (40 mL) for crystallization by slow diffusion. Red crystals were isolated by filtration and dried under vacuum. The supernatant liquid was concentrated and layered with fresh pentane to yield a second crop of product (537 mg total, 74%); mp >250 °C; μ_{eff} = 3.70 μ_B; IR (Nujol, KCl) ν_{CO} = 1885 cm^{-1}. Anal.

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Calcd for $C_{48}H_{60}CoCrN_4O_6$: C, 64.06; H, 6.72; N, 6.23. Found: C, 63.75; H, 6.69; N, 6.21.

Crystallography of 1. X-ray quality crystals were grown by diffusion of pentane into a saturated solution of **1** in THF at room temperature. A dark-red crystal (0.40 × 0.30 × 0.20 mm) was mounted on a glass capillary using Paratone-N hydrocarbon oil, transferred to a Siemens SMART[85] 1000 diffractometer/CCD area detector, and cooled to a temperature of −100 °C using a calibrated nitrogen-flow low-temperature apparatus. A primitive triclinic unit cell was determined from a least-squares refinement on data from 60 sample frames. An arbitrary hemisphere of data was collected using 0.3° ω-scans that were collected for a total of 30 s per frame. The data were integrated by SAINT[86] to a maximum 2θ value of 46.5°, and the final unit cell parameters were determined by a least-squares analysis of 6781 reflections with $I > 2\sigma(I)$. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. An absorption correction was performed using SADABS[87] (T_{max} = 0.879, T_{min} = 0.778).

Of the 31 499 reflections that comprised the hemisphere, 12 902 were unique (R_{int} = 0.097), and the equivalent reflections were averaged. The structure was solved by direct methods[88] and expanded using Fourier techniques,[89] using SHELX 97.[90] Within the two molecules of **1** that make up the asymmetric unit, two THF ligands and one ethyl group were disordered. Excluding the disordered carbon atoms, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as fixed atoms but not refined. The final cycle of full-matrix least squares refinement was based on 12 902 observed reflections and 1277 variable parameters and converged with final residuals:[91] R = 0.064, R_w = 0.137, and GOF = 0.948. The analytical forms of the scattering factor tables for the neutral atoms were used,[92] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[93]

3,4-Epoxybutyl Butyrate (48). A 500 mL round-bottomed flask was charged with 3-buten-1-ol (16.2 g, 225 mmol), toluene (150 mL), and triethylamine (35 mL). After cooling to 0 °C, butyryl chloride (25 mL, 25.5 g, 238 mmol) was added dropwise via an addition funnel. The reaction mixture was stirred at 0 °C for 2 h and then allowed to warm to ambient temperature overnight. After filtration, the toluene solution was washed three times with H_2O (100 mL) and twice with brine (100 mL). After drying over $MgSO_4$, the solvent was removed under vacuum to yield 3-butenyl butyrate as a crude oil. This oil was placed in a 2 L round-bottomed flask and dissolved in CH_2Cl_2 (700 mL). After cooling to 0 °C, *m*-chloroperoxybenzoic acid (77% purity (Aldrich), 81 g, 360 mmol) was added in portions over 20 min. The ice bath was removed after 1 h, and the reaction was left to stir overnight. Excess peroxide was quenched by the slow addition of 10% $NaHSO_3$(aq) (400 mL) at 0 °C, followed by slow addition of $NaHCO_3$-(aq) (sat.) until bubbling ceased. The product was extracted three times with CH_2Cl_2 (200 mL) and washed with $NaHCO_3$(aq) (sat., 400 mL) and brine (3 × 400 mL). The organic phase was dried over $MgSO_4$ and the solvent removed in vacuo, leaving behind the product as a crude oil. Purification by distillation under reduced pressure (10 mmHg) yielded the desired product as a colorless liquid (16.2 g, 46%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.135 (t, 2H, ^3J = 6 Hz), 2.919 (dddd, 1H, ^3J = 6 Hz, ^3J = 5 Hz, ^3J = 4 Hz, ^3J = 3 Hz), 2.690 (dd, 1H, ^2J = 5 Hz, ^3J = 4 Hz), 2.417 (dd, 1H, ^2J = 5 Hz, ^3J = 3 Hz), 2.209 (t, 2H, ^3J = 7 Hz), 1.837 (dtd, 1H, ^2J = 14 Hz, ^3J = 6 Hz, ^3J = 5 Hz), 1.720 (dq, 1H, ^2J = 14 Hz, ^3J = 6 Hz), 1.566 (sext, 2H, ^3J = 7 Hz), 0.860 (t, 3H, ^3J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.6, 61.2, 49.7, 46.9, 36.2, 32.1, 18.5, 13.8; IR (neat, KCl) ν_{CO} = 1738 cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_8H_{14}O_3$) 158.0943, found 158.0937.

4,5-Epoxypentyl Butyrate (50). Procedure analogous to that of 3,4-epoxybutyl butyrate, substituting 4-penten-1-ol for 3-buten-1-ol: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.025 (td, 2H, ^3J = 6 Hz, ^4J = 1.5 Hz), 2.843 (mult, 1H), 2.662 (dd, 1H, ^2J = 5 Hz, ^3J = 4 Hz), 2.385 (dd, 1H, ^2J = 5 Hz, ^3J = 3 Hz), 2.186 (t, 2H, ^3J = 8 Hz), 1.707 (mult, 2H), 1.63−1.43 (mult, 2H), 1.553 (sext, 2H, ^3J = 8 Hz), 0.850 (t, 3H, ^3J = 8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.6, 63.7, 51.7, 47.0, 36.2, 29.1, 25.2, 18.5, 13.7; IR (neat, KCl) ν_{CO} = 1737 cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_9H_{16}O_3$ + H$^+$) 173.1178, found 173.1179.

Propyl 4,5-Epoxypentanoate (52). Procedure analogous to that of 3,4-epoxybutyl butyrate, substituting *n*-propanol for 3-buten-1-ol and 4-pentenoyl chloride for butyryl chloride: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.979 (t, 2H, ^3J = 7 Hz), 2.921 (mult, 1H), 2.698 (dd, 1H, ^3J = 5 Hz, ^3J = 4 Hz), 2.442 (dd, 1H, ^3J = 5 Hz, ^3J = 2.4 Hz), 2.400 (t, 2H, ^3J = 8 Hz), 1.907 (mult, 1H), 1.712 (sext, 1H, ^3J = 7 Hz), 1.588 (sext, 2H, ^3J = 7 Hz), 0.876 (t, 3H, ^3J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.1, 66.3, 51.4, 47.2, 30.6, 27.8, 22.1, 10.5; IR (neat, KCl) ν_{CO} = 1736 cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_8H_{14}O_3$ + H$^+$) 159.1021, found 159.1017.

General Procedure for the Carbonylation of Epoxides. Carbonylations were carried out with 150−500 mg of epoxide. Substrate: catalyst ratios are accurate to within 5%. Under nitrogen at room temperature, a 4-mL glass vial equipped with a stir bar was charged with catalyst followed by epoxide. This was immediately transferred to a custom-built, 6-well, high-pressure reactor.[30] The reactor was pressurized to 900 psi with CO and heated to 60 °C with stirring. The temperature was held constant for 6 h, at which point the reactor was submerged in dry ice for 15 min. After careful venting of excess CO, the glass vial was removed and product yield determined by ^{1}H NMR. Pure lactones were isolated by careful vacuum distillation, unless noted below.

Characterization of Lactones. 4-(Methoxymethyl)-2-propiolactone (18): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.644 (dddd, 1H, ^3J = 6 Hz, ^3J = 5 Hz, ^3J = 5 Hz, ^3J = 3 Hz), 3.739 (dd, 1H, ^2J = 11 Hz, ^3J = 3 Hz), 3.635 (dd, 1H, ^2J = 11 Hz, ^3J = 5 Hz), 3.463 (dd, 1H, ^2J = 16 Hz, ^3J = 6 Hz), 3.431 (s, 3H), 3.379 (dd, 1H, ^2J = 16 Hz, ^3J = 5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.9, 72.1, 69.6, 59.8, 39.7; IR (neat, KCl) ν_{CO} = 1827 cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_5H_8O_3$) 116.0473, found 116.0476.

4-(Furfuryloxymethyl)-2-propiolactone (26): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.416 (dd, 1H, ^3J = 1.5 Hz, ^3J = 1.5 Hz), 6.351 (d, 2H, ^3J = 1.5 Hz), 4.634 (dddd, 1H, ^3J = 6 Hz, ^3J = 5 Hz, ^3J = 5 Hz, ^3J = 3 Hz), 4.575 (d, 1H, ^2J = 13 Hz), 4.516 (d, 1H, ^2J = 13 Hz), 3.812 (dd, 1H, ^2J = 12 Hz, ^3J = 3 Hz), 3.711 (dd, 1H, ^2J = 12 Hz, ^3J = 5 Hz), 3.448 (dd, 1H, ^2J = 16 Hz, ^3J = 6 Hz), 3.363 (dd, 1H, ^2J = 16 Hz, ^3J = 5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8, 151.1, 143.2, 110.5, 110.1, 69.4, 69.2, 65.5, 39.9; IR (neat, KCl) ν_{CO} = 1826 cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_9H_{10}O_4$) 182.0579, found 182.0578.

4-(Allyloxymethyl)-2-propiolactone (28): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.885 (ddt, 1H, ^3J = 17 Hz, ^3J = 10 Hz, ^3J = 6 Hz), 5.286 (ddt, 1H, ^3J = 17 Hz, ^2J = 1.5 Hz, ^4J = 1.5 Hz), 5.213 (ddt, 1H, ^3J = 10 Hz, ^2J = 1.5 Hz, ^4J = 1.5 Hz), 4.655 (dddd, 1H, ^3J = 6 Hz, ^3J = 5 Hz, ^3J = 5 Hz, ^3J = 3 Hz), 4.068 (mult, 2H), 3.790 (dd, 1H, ^2J = 12 Hz, ^3J = 3 Hz), 3.688 (dd, 1H, ^2J = 12 Hz, ^3J = 5 Hz), 3.472 (dd, 1H,

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(91) $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$, $R_w = [(\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w\, F_o^2)]^{1/2}$, GOF = $[\Sigma\, w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables, and the weight $w = 4\,F_o^2/\sigma^2(F_o)^2 = [\sigma^2(F_o) + (pF_o/2)^2]^{-1}$ and p is the factor used to lower the weight of intense reflections.
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^2J = 16 Hz, ^3J = 6 Hz), 3.398 (dd, 1H, ^2J = 16 Hz, ^3J = 5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.9, 134.1, 117.7, 72.7, 69.5, 69.3, 39.7; IR (neat, KCl) ν_{CO} = 1827 cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_7H_{10}O_3$ + H^+) 143.0708, found 143.0706.

4-(Acetoxymethyl)-2-propiolactone (40): Isolated by column chromatography (silica/$CHCl_3$): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.698 (dddd, 1H, ^3J = 6 Hz, ^3J = 5 Hz, ^3J = 4 Hz, ^3J = 3 Hz), 4.449 (dd, 1H, ^2J = 13 Hz, ^3J = 3 Hz), 4.203 (dd, 1H, ^2J = 13 Hz, ^3J = 5 Hz), 3.525 (dd, 1H, ^2J = 16 Hz, ^3J = 6 Hz), 3.296 (dd, 1H, ^2J = 16 Hz, ^3J = 4 Hz), 2.066 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.7, 167.2, 67.9, 63.6, 40.3, 20.8; IR (neat, KCl) ν_{CO} = 1832 (lactone), 1743 (acetyl) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_6H_8O_4$ + H^+) 145.0501, found 145.0504.

4-(Butyroxymethyl)-2-propiolactone (42): Isolated by column chromatography (silica/$CHCl_3$): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.711 (dddd, 1H, ^3J = 6 Hz, ^3J = 5 Hz, ^3J = 4 Hz, ^3J = 3 Hz), 4.497 (dd, 1H, ^2J = 13 Hz, ^3J = 3 Hz), 4.241 (dd, 1H, ^2J = 13 Hz, ^3J = 5 Hz), 3.537 (dd, 1H, ^2J = 16 Hz, ^3J = 6 Hz), 3.317 (dd, 1H, ^2J = 16 Hz, ^3J = 4 Hz), 2.335 (t, 2H, ^3J = 7 Hz), 1.644 (sext, 2H, ^3J = 7 Hz), 0.931 (t, 3H, ^3J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.3, 166.9, 67.9, 63.3, 40.4, 36.0, 18.5, 13.8; IR (neat, KCl) ν_{CO} = 1831 (lactone), 1738 (butyryl) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_8H_{12}O_4$ + H^+) 173.0814, found 173.0809.

(*R*)-4-(Butyroxymethyl)-2-propiolactone ((*R*)-42): Isolated by column chromatography (silica/$CHCl_3$): $[\alpha]^{21}_D$ −38.4° (*c* = 1.14, $CHCl_3$).

4-(Benzoyloxymethyl)-2-propiolactone (44): Isolated by column chromatography (silica/$CHCl_3$): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.035 (d, 2H, ^3J = 8 Hz), 7.589 (t, 1H, ^3J = 8 Hz), 7.451 (t, 2H, ^3J = 8 Hz), 4.866 (dddd, 1H, ^3J = 6 Hz, ^3J = 5 Hz, ^3J = 4 Hz, ^3J = 3 Hz), 4.726 (dd, 1H, ^2J = 13 Hz, ^3J = 3 Hz), 4.540 (dd, 1H, ^2J = 13 Hz, ^3J = 5 Hz), 3.630 (dd, 1H, ^2J = 17 Hz, ^3J = 6 Hz), 3.439 (dd, 1H, ^2J = 17 Hz, ^3J = 4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.0, 166.2, 133.8, 130.0, 129.3, 128.8, 68.0, 64.0, 40.5; IR (neat, KCl) ν_{CO} = 1833 (lactone), 1723 (benzoyl) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_{11}H_{10}O_4$) 206.0579, found 206.0584.

***β*-Butyroxy-*γ*-butyrolactone (46):**[94] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.404 (dd, 1H, ^3J = 7 Hz, ^3J = 5 Hz), 4.481 (dd, 1H, ^2J = 11 Hz, ^3J = 5 Hz), 4.313 (d, 1H, ^2J = 11 Hz), 2.837 (dd, 1H, ^2J = 18 Hz, ^3J = 7 Hz), 2.553 (d, 1H, ^2J = 18 Hz), 2.282 (t, 2H, ^3J = 7 Hz), 1.616 (sext, 2H, ^3J = 7 Hz), 0.913 (t, 3H, ^3J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.9, 173.2, 73.4, 69.8, 36.0, 34.8, 18.4, 13.8; IR (neat, KCl) ν_{CO} = 1789 (lactone), 1738 (butyryl) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_8H_{12}O_4$ + H^+) 173.0814, found 173.0812.

(*S*)-*β*-Butyroxy-*γ*-butyrolactone ((*S*)-46): Method a. Synthesized as previously reported, by reaction of butyryl chloride with (*S*)-*β*-hydroxy-*γ*-butyrolactone;[94] $[\alpha]^{21}_D$ −77.8° (*c* = 1.02, $CHCl_3$). **Method b.** Carbonylation of (*R*)-glycidyl butyrate ((*R*)-**41**) using catalyst **1**; $[\alpha]^{21}_D$ −78.8° (*c* = 0.99, $CHCl_3$).

***β*-Benzoyloxy-*γ*-butyrolactone (47):** Isolated by recrystallization from ethanol at −30 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.021 (d, 2H, ^3J = 7 Hz), 7.603 (t, 1H, ^3J = 7 Hz), 7.458 (dd, 2H, ^3J = 7 Hz, ^3J = 7 Hz), 5.686 (ddt, 1H, ^3J = 7 Hz, ^3J = 5 Hz, ^3J = 1.5 Hz), 4.622 (dd, 1H, ^2J = 11 Hz, ^3J = 5 Hz), 4.521 (dd, 1H, ^2J = 11 Hz, ^3J = 1.5 Hz), 2.978 (dd, 1H, ^2J = 18 Hz, ^3J = 7 Hz), 2.776 (dd, 1H, ^2J = 18 Hz, ^3J = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.8, 166.1, 134.0, 130.0, 129.1, 128.8, 73.4, 70.5, 34.9; IR (Nujol, KCl) ν_{CO} = 1771 (lactone), 1716 (benzoyl) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_{11}H_{10}O_4$) 206.0579, found 206.0576.

(94) The synthesis, IR spectrum, boiling point, and refractive index of **46** have previously been reported: van Tamelen, E. E.; Strong, F. M.; Quarck, U. C. *J. Am. Chem. Soc.* **1959**, *81*, 750−751.

4-(2-Butyroxyethyl)-2-propiolactone (49): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.584 (dtd, 1H, ^3J = 8 Hz, ^3J = 6 Hz, ^3J = 4.5 Hz), 4.24−4.08 (mult, 2H), 3.540 (dd, 1H, ^2J = 17 Hz, ^3J = 6 Hz), 3.124 (dd, 1H, ^2J = 17 Hz, ^3J = 4.5 Hz), 2.235 (t, 2H, ^3J = 7 Hz), 2.105 (mult, 2H), 1.588 (sext, 2H, ^3J = 7 Hz), 0.888 (t, 3H, ^3J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.6, 167.9, 68.7, 60.1, 43.5, 36.2, 34.0, 18.5, 13.8; IR (neat, KCl) ν_{CO} = 1828 (lactone), 1735 (butyryl) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_9H_{14}O_4$ + H^+) 187.0970, found 187.0966.

4-(3-Butyroxypropyl)-2-propiolactone (51): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.535 (dtd, 1H, ^3J = 8 Hz, ^3J = 6 Hz, ^3J = 4 Hz), 4.113 (td, 2H, ^3J = 6 Hz, ^4J = 2 Hz), 3.538 (dd, 1H, ^2J = 16 Hz, ^3J = 6 Hz), 3.079 (dd, 1H, ^2J = 16 Hz, ^3J = 4 Hz), 2.276 (t, 2H, ^3J = 7 Hz), 1.93−1.72 (mult, 4H), 1.639 (sext, 2H, ^3J = 7 Hz), 0.935 (t, 3H, ^3J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.8, 168.2, 70.9, 63.4, 43.2, 36.3, 31.7, 24.6, 18.6, 13.9; IR (neat, KCl) ν_{CO} = 1828 (lactone), 1732 (butyryl) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_{10}H_{16}O_4$ + H^+) 201.1127, found 201.1122.

Propyl 3-(4-oxo-oxetan-2-yl)propionate (53): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.584 (dddd, 1H, ^3J = 7 Hz, ^3J = 6 Hz, ^3J = 5 Hz, ^3J = 4 Hz), 4.045 (t, 2H, ^3J = 7 Hz), 3.551 (dd, 1H, ^2J = 16 Hz, ^3J = 6 Hz), 3.111 (dd, 1H, ^2J = 16 Hz, ^3J = 4 Hz), 2.497 (dd, 1H, ^3J = 7 Hz, ^2J = 4 Hz), 2.471 (dd, 1H, ^3J = 7 Hz, ^2J = 4 Hz), 2.162 (dtd, 1H, ^2J = 22 Hz, ^3J = 7 Hz, ^3J = 5 Hz), 2.075 (dq, 1H, ^2J = 22 Hz, ^3J = 7 Hz), 1.648 (sext, 2H, ^3J = 7 Hz), 0.933 (t, 3H, ^3J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.5, 167.9, 70.3, 66.7, 43.2, 30.2, 29.8, 22.1, 10.6; IR (neat, KCl) ν_{CO} = 1828 (lactone), 1731 (butyryl) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_9H_{14}O_4$ + H^+) 187.0970, found 187.0972.

***N*,*N*-Dimethyl-9-(4-oxo-oxetan-2-yl)nonamide (55):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.496 (dtd, 1H, ^3J = 7 Hz, ^3J = 6 Hz, ^3J = 4 Hz), 3.502 (dd, 1H, ^2J = 16 Hz, ^3J = 6 Hz), 3.048 (dd, 1H, ^2J = 16 Hz, ^3J = 4 Hz), 2.997 (s, 3H), 2.936 (s, 3H), 2.296 (t, 2H, ^3J = 8 Hz), 1.9−1.7 (mult, 2H), 1.617 (pent, 2H, ^3J = 8 Hz), 1.313 (br, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.4, 168.7, 71.5, 43.1, 37.5, 35.5, 34.8, 33.5, 29.6, 29.5, 29.4, 29.3, 25.3, 25.1; IR (neat, KCl) ν_{CO} = 1812 (lactone), 1644 (amide) cm^{-1}; HRMS (EI) *m*/*z* calcd ($C_{14}H_{25}NO_3$) 255.1834, found 255.1839.

Isomerization of Allyl Glycidyl Carbonate (56). Under nitrogen at room temperature, a 4-mL glass vial equipped with a stir bar was charged with **1** (3 mg, 4.0 μmol) followed by allyl glycidyl carbonate (**56**, 157 mg, 0.99 mmol, 250 equiv). This was immediately transferred to a custom-built, 6-well, high-pressure reactor.[30] The reactor was pressurized to 900 psi with CO and heated to 60 °C with stirring. The temperature was held constant for 6 h, at which point the reactor was submerged in dry ice for 15 min. After careful venting of excess CO, the glass vial was removed. ^{1}H NMR confirmed quantitative conversion to 4-allyloxymethyl-1,3-dioxolan-2-one (**57**) by comparison with previously reported spectroscopy.[68]

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Supporting Information Available: Table of product distributions for various substrate/catalyst ratios in the carbonylation of cyclododecene oxide and crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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