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Pressure Dependence of the Carbon Dioxide/Cyclohexene Oxide Coupling Reaction Catalyzed by Chromium Salen Complexes. Optimization of the Comonomer-Alternating Enchainment Pathway

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The rate of the copolymerization reaction of cyclohexene oxide and carbon dioxide in the presence of (salen)$Cr^{III}N_3$ and various cocatalysts has been determined as a function of CO_2 pressure. Carbon dioxide insertion into the (salen)Cr-alkoxide intermediates, afforded following epoxide ring-opening, was shown to be rate-limiting at pressures below 35 bar. Higher pressures of carbon dioxide resulted in catalyst/substrate dilution with a concomitant decrease in the rate of copolymer formation. On the other hand, cyclic carbonate formation was inhibited as the CO_2 pressure was increased. The most active (salen)CrN_3 catalyst (H_2-salen = *N*,*N*′-bis(3-*tert*-butyl-5-methoxysalicylidene)-(1*R*,2*R*)-cyclohexenediimine), along with a [PPN][N_3] cocatalyst, exhibited a TOF of 1153 mol epoxide consumed/mol chromium·h at 80 °C and a CO_2 pressure of 34.5 bar.

Introduction

The copolymerization of CO_2 and epoxides is widely regarded as a process worthy of intense scrutiny since it not only utilizes CO_2 as a C_1 feedstock but also provides a *green* route to polycarbonates,[1] thermoplastics currently commercially produced by condensation polymerization of diols and phosgene or carbonates.[2] Although zinc has long been the metal of choice for designing both heterogeneous and homogeneous catalysts for this reaction, other metal catalysts have recently been exploited for this process.[3] Prominent among these are porphyrin and bis(salicylaldimine) derivatives of cobalt,[4] aluminum,[5] and chromium,[6] with the latter complexes being the most efficient for selective coupling of both *alicyclic* and *aliphatic* epoxides with CO_2 to provide polycarbonates. Mechanistic studies aided by in situ infrared monitoring of the copolymerization process involving cyclohexene oxide as comonomer have addressed the optimization of the salen ligand, the initiator, and the cocatalyst.[6g] These investigations have led to a 50-fold enhancement in the overall rate of copolymer production over our initially reported results.[6d] Herein, we wish to describe the effects of carbon dioxide pressure upon the activity and selectivity of the comonomer-alternating enchainment process utilizing complexes **1** and **2** (Figure 1) as catalysts, along with various cocatalysts.

Due to the high Lewis acidity of zinc complexes and their concomitant affinity for ring-opening epoxides, our early investigations utilizing these catalysts for the copolymerization of epoxides and CO_2 were performed at high CO_2 pressures.[7] That is, these processes required

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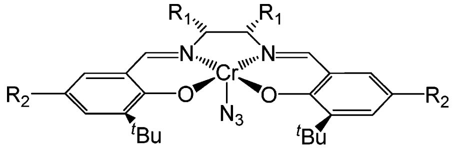

1: R_1 = H, R_2 = *t*-Bu
2: R_1 = (1R, 2R)-C_4H_8-, R_2 = OCH_3

Figure 1. Skeletal representation of chromium salen catalysts.

Table 1. Effect of CO_2 Pressure on the Rate of Copolymerization Employing *N*-Methylimidazole as a Cocatalyst[a]

CO_2 pressure (bar)	% carbonate[b]	TON[c]	TOF[d]
6.90	94.5	230.4	23.0
13.8	97.4	466.6	46.7
20.7	97.6	564.5	56.5
27.6	98.5	622.1	62.2
34.5	98.3	669.9	67.0
41.4	98.1	492.1	49.2
55.2	97.8	444.4	44.4

[a] Copolymerization reactions performed with 50 mg (0.0855 mmol) of catalyst **1** and 2.25 equiv of *N*-methylimidazole in 20 mL (0.198 mol) of cyclohexene oxide at 80 °C for 10 h. [b] Estimated by ^{1}H NMR. [c] Mol epoxide consumed/mol catalyst. [d] Mol epoxide consumed/mol catalyst·h.

a high CO_2 concentration in order to avoid a sizable percentage of polyether linkages in the thus formed copolymer. In related studies Coates and co-workers have reported that zinc β-diiminates produce copolymer at a large TOF at 6.9 bar CO_2; however, the carbonate content of the copolymer was only 90%.[8] Unlike these zinc catalysts, our (salen)Cr^{III}X-catalyzed systems are ineffective at homopolymerization of epoxides to polyethers; hence, these processes should not require high CO_2 pressure in order to minimize polyether linkages. Indeed, studies employing catalyst **1** in the presence of *N*-methylimidazole as a cocatalyst showed that the carbonate content of the copolymer was only slightly enhanced via the use of high pressures of carbon dioxide (Table 1).

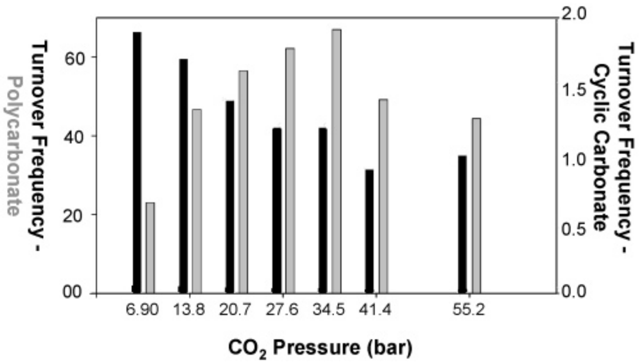

Figure 2. Graphical representation of the CO_2 pressure dependence of the rates of copolymer and cyclic carbonate production.

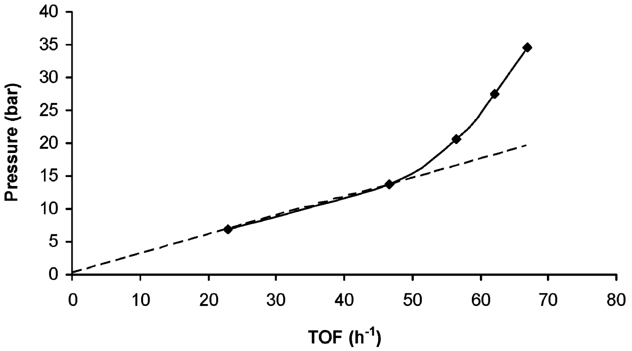

Figure 3. Pressure dependence of TOF for polycarbonate production at 80 °C utilizing complex **1** as catalyst and 2.25 equiv of *N*-MeIm as cocatalyst.

On the other hand, the rate of copolymerization varied significantly with pressure. That is, an increase of CO_2 pressure from 6.90 to 34.5 bar resulted in a 3-fold enhancement in the rate of copolymer formation. It should be noted here that the phase behavior of the cyclohexene oxide/carbon dioxide binary has been described by Super and Beckman.[9] Over the CO_2 pressure range of this study there exists a dense cyclohexene oxide-rich phase and a CO_2-rich phase. Since catalysts **1** and **2** are insoluble in CO_2, the catalyst resides in the cyclohexene oxide-rich phase. Our investigations were carried out with a constant charge of cyclohexene oxide to the reactor, and the amount of CO_2 added increases as the pressure increases. Contrary to the dependence of the rate of copolymer formation with pressure, the rate of cyclic carbonate formation exhibited an inverse trend, increasing at lower CO_2 pressures. Figure 2 illustrates the effect of CO_2 pressure on the production of the two products of the CO_2/cyclohexene oxide coupling reaction. It is apparent from this graphical representation that the reaction is highly selective for copolymer production. Furthermore, as apparent from Figure 3, over the P_{CO_2} range where Henry's law is applicable (<15 bar) the rate of copolymer production is first-order in [CO_2].[10] Increasing the carbon dioxide pressure beyond 35 bar has the effect of decreasing the rate of copolymer production. This is the result of a simple catalyst/epoxide dilution effect on reaction rate, where upon increasing the CO_2 pressure greater than 35 bar, there is a major volumetric expansion of the liquid phase where the catalyst and epoxide reside.[11]

These observations are readily accounted for in Scheme 1, in that high concentrations of CO_2 increase the rate of carbonate formation (pathway A), thereby reducing the lifetime of the alkoxide intermediate necessary for the back-biting mechanism (pathway B) for cyclic carbonate production. A similar trend has been observed by Rieger and co-workers for the copolymerization of propylene oxide and CO_2, where propylene carbonate production decreased with increasing CO_2

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Scheme 1

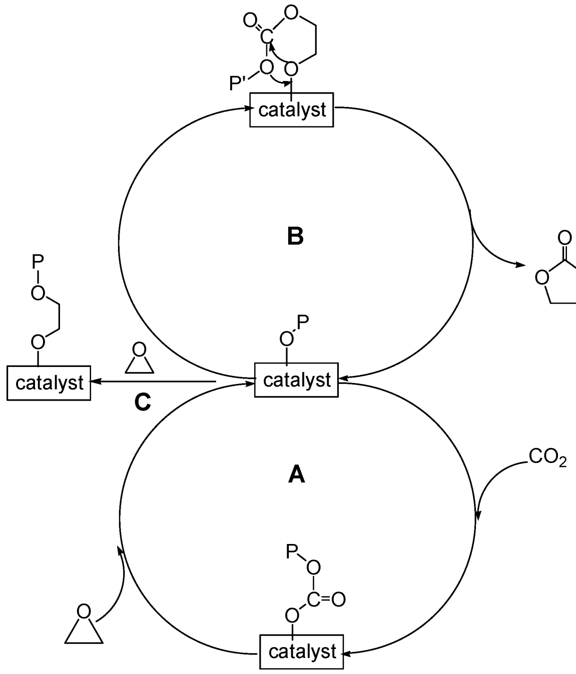

Table 2. Effect of CO$_2$ Pressure on the Rate of Copolymerization Utilizing Tricyclohexylphosphine as a Cocatalyst[a]

CO$_2$ pressure (bar)	% carbonate[b]	TON[c]	TOF[d]
0	0	Very little polyether	
1.00	89.5	82.4	6.9
6.90	98.4	593.0	59.3
34.5	98.9	1002.1	250.5
55.2	>99	391.0	98.0

[a] Copolymerization reactions performed with 50 mg (0.0855 mmols) of catalyst **1** and 3 equivalents tricyclohexylphosphine in 20 mL (0.198 mols) of cylcohexene oxide at 80°C. [b] Estimated by ^{1}H NMR. [c] Mols epoxide consumed/mol catalyst. [d] Mol epoxide consumed/mol catalyst·h.

pressure.[12] As indicated in Table 1, pathway C leading to polyether linkages is not of much consequence in this instance.

Further copolymerization studies employing catalyst **1**, but with the more effective cocatalyst, tricyclohexylphosphine, have shown a similar dependence on CO$_2$ pressure (Table 2). In this case even CO$_2$ pressures as low as *one* atmosphere produced copolymer with ~90% carbonate linkages, albeit at a significantly reduced rate. Indeed, this represents only the second instance where this process has been reported to occur at such a low carbon dioxide pressure.[13] Surprisingly, attempts to preclude CO$_2$ from the polymer resulted in very little product formation. That is, the catalyst system was not effective at homopolymerizing cyclohexene oxide. This leads us to the conclusion that epoxide ring opening is disfavored when a metal-bound alkoxide is present, but favored when following CO$_2$ insertion. This result accounts for the consistently high CO$_2$ content in the copolymer produced and further supports the conclusions that CO$_2$ insertion plays a role in determining the rate of copolymerization at least at low CO$_2$ pressures.

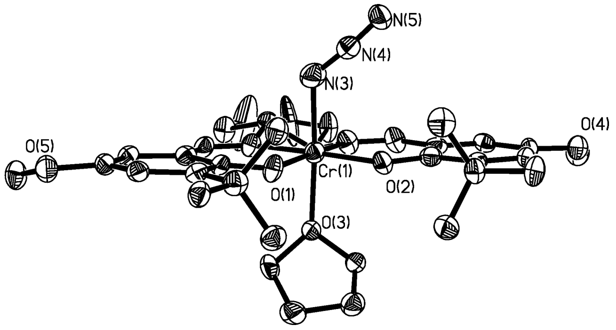

Figure 4. Molecular structure of catalyst **2**·THF. Ellipsoids are shown at the 50% probability level, hydrogens are omitted for clarity. Selected distances (Å) and angles (deg): Cr(1)–N(3), 1.992(7); Cr(1)–O(3), 2.093(5); Cr(1)–O(1), 1.899(5); Cr(1)–O(2), 1.914(5); Cr(1)–N(1), 2.000(6); Cr(1)–N(2), 1.997(6); N(3)–N(4), 1.210(9); N(4)–N(5), 1.144(8); Cr(1)–N(3)–N(4), 127.5(5); N(3)–N(4)–N(5), 174.5(8).

Table 3. Effects of Altering the CO$_2$ Pressure on the Rate of Copolymerization of Catalyst 2 and PPN$^+$Cl$^-$ Cocatalyst[a]

CO$_2$ pressure (bar)	% carbonate[b]	TON[c]	TOF[d]
6.90		495.8	495.8
34.5	>99	2462.4	1056.8
55.2	>99	1768.3	442.1
34.5[e]	>99	2685.5	1152.6

[a] Copolymerization reactions performed with 50 mg (0.0852 mmol) of catalyst **2** and 1 equiv of PPNCl in 20 mL (0.198 mol) of cyclohexene oxide at 80 °C. [b] Estimated by ^{1}H NMR. [c] Mol epoxide consumed/mol catalyst. [d] Mol epoxide consumed/mol catalyst·h. [e] Copolymerization performed with 1 equiv of PPNN$_3$, $M_n = 50\,000$ and PDI = 1.13.

By way of contrast with the previous set of experiments employing *N*-MeIm as cocatalyst, in the presence of PCy$_3$ as cocatalyst complex **1** affords only trace quantities of cyclic carbonate below 14 bar CO$_2$ pressure. At higher pressures of CO$_2$ the reaction is completely selective for copolymer formation.

Finally, the copolymerization process has been optimized utilizing our most effective catalyst/cocatalyst combination, namely, complex **2** and bis(triphenylphosphoranylidene)ammonium (PPN$^+$) salts, and altering the CO$_2$ pressure. The crystal structure of **2**·THF is illustrated in Figure 4. This complex contains a bis(salicylaldimine) ligand which has electron-donating methoxy groups and solubilizing *tert*-butyl groups in the *para* and *ortho* positions of the phenolate moiety, respectively, along with a chiral cyclohexyl backbone and a highly nucleophilic azide initiator. The rate of copolymerization for this system is very fast at 6.90 bar; however, the reaction quickly slows down due to a depletion of CO$_2$ in solution. This is evident as shown by in situ infrared spectroscopy, where the absorbance due to CO$_2$ drops significantly during a catalytic run carried out under these conditions, making higher pressures necessary to obtain the maximum rate of catalysis (Table 3). As shown before, a rather dramatic increase in rate is observed upon increasing the CO$_2$ pressure to 34.5 bar, obtaining a maximum rate of 1056.8 mol epoxide consumed/mol catalyst·h with PPN$^+$Cl$^-$ as a cocatalyst, and a slightly higher rate of 1152.6 mol epoxide consumed/mol catalyst·h in the presence of PPN$^+$N$_3$$^-$ as a cocatalyst.

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Summary Remarks

In conclusion, several simple modifications of the (salen)$Cr^{III}X$ catalyst have had dramatic effects on the rate of copolymerization of cyclohexene oxide and CO_2. These include exchanging a *tert*-butyl substituent on the phenolate moiety with methoxy, the initiator X from chloride to azide, in addition to employing an optimum CO_2 pressure. As a result, this chromium catalyst (**2**) in the presence of [PPN][N_3] as a cocatalyst represents the best performing catalyst system we have developed to date for this copolymerization reaction. That is, complex **2** along with an equivalent of [PPN][N_3] provides a TOF of 1153 h^{-1} at 80 °C and a CO_2 pressure of 34.5 bar. Furthermore, the afforded copolymer has a M_n of 50 000 with a PDI of 1.13. Complex **2** in the presence of PCy_3 as cocatalyst, although not as active as in the presence of [PPN][N_3], is 100% selective for copolymer production at modest pressures of CO_2. These studies have addressed several mechanistic aspects of this process. For example, although we have shown that low-valent metal alkoxides insert CO_2 very fast,[14] CO_2 insertion into the (salen)Cr^{III}-alkoxide intermediate can be rate limiting at low CO_2 pressures. On the other hand, high CO_2 pressures, greater than 35 bar but less than supercritical conditions, simply swell the epoxide-rich phase which contains the catalyst/substrate and retards the rate of copolymerization via a dilution effect. Finally, we observed that the (salen)Cr^{III}-alkoxide intermediate is very reluctant to ring-open an epoxide prior to CO_2 insertion, thereby leading to completely comonomer-alternating enchainment. This observation is of course a very desirable feature of this catalyst system.

Experimental Section

Methods and Materials. Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. Cyclohexene oxide (Lancaster) was freshly distilled from CaH_2, *N*-methylimidazole (Aldrich) was distilled over sodium metal prior to use, and $AgClO_4$ (Strem) was used without further purification. Bone dry carbon dioxide supplied in a high-pressure cylinder equipped with a liquid dip-tube was purchased from Scott Specialty Gases. 3,5-Di-*tert*-butylsalicylaldehyde[15] and 3-*tert*-butyl-5-methoxysalicylaldehyde[16] were synthesized as described in the literature. Unless otherwise stated, all other reagents were used without further purification. Infrared spectra were recorded on a Mattson 6021 FT-IR spectrometer with DTGS and MCT detectors. Ligand and complex syntheses have been reported elsewhere by us, and here we report a summary of those findings.[6j]

Synthesis of *N,N′*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine. Ethylenediamine, 3,5-di-*tert*-butylsalicylaldehyde, and a few drops of aqueous formic acid were dissolved in methanol and heated to reflux for 2 h. The precipitated product was filtered and washed with small aliquots of cold methanol, producing a yellow solid (~60% yield).

Synthesis of *N,N′*-Bis(3-*tert*-butyl-5-methoxysalicylidene)-(1*R*,2*R*)-cyclohexenediimine. (1*R*,2*R*)-(+)-1,2-Diaminocyclohexane L-tartrate, K_2CO_3, and distilled H_2O were stirred until complete dissolution was observed. Ethanol was then added and the solution was heated to reflux (75−80 °C). 3-*tert*-Butyl-5-methoxysalicylaldehyde dissolved in ethanol was added, and the reaction was allowed to stir for 2 h. Water was added, causing the ligand to precipitate out of solution. The product was collected by vacuum filtration, washed with cold ethanol, and dried in vacuo, yielding a yellow solid (~80% yield).

General Synthesis of Cr^{III}(salen)Cl Complexes. Salicylaldimine (1.0 equiv) and chromium(II) chloride (1.1 equiv) were dissolved in THF and stirred under argon at ambient temperature for 24 h. The reaction mixture then was exposed to air and stirred an additional 24 h. After diluting the reaction mixture with diethyl ether, the organic layer was washed with aqueous saturated NH_4Cl and brine solutions followed by drying with Na_2SO_4. After filtration the solvent was removed in vacuo, yielding a dark brown powder.

General Synthesis of Cr^{III}(salen)N_3 Complexes. The procedure previously reported by Jacobsen was followed.[17] The desired amount of Cr(salen)Cl complex was first dissolved in CH_3CN. In another Schlenk flask equipped with a pressure-equalizing addition funnel, 1 equiv of $AgClO_4$ was dissolved in an equal volume of CH_3CN. The Cr(salen)Cl solution was cannulated into the addition funnel and added dropwise. Immediate precipitation of AgCl was observed, and the reaction was allowed to stir overnight. The mixture was filtered using a Büchner funnel (**NOTE:** perchlorate salts are potentially explosive and should not be used with fritted filters), and 3 equiv of NaN_3 was added, keeping exposure to air at a minimum. The reaction was allowed to stir for 24 h, and the mixture was diluted with diethyl ether. The organic portion was washed with water to remove $NaClO_4$ and excess NaN_3 and dried with Na_2SO_4, and the solvent was removed in vacuo. This “impure azide” was dissolved in diethyl ether, along with 10 equiv of azidotrimethylsilane. The reaction was allowed to stir for 8 h and the solvent removed. The solid was washed with several small aliquots of diethyl ether and filtered to yield a dark brown powder in 65% yield. Anal. Calcd (%) for $C_{36}H_{46}N_5O_2Cr$: C, 65.73; H, 7.93; N, 11.98. Found (impure): C, 64.85; H, 7.81; N, 8.95. Found (purified): C, 65.51; H, 7.72; N, 11.93.

Copolymerization of Epoxides and CO_2. With the exception of the PPN^+ salts, the cocatalysts were added as neat solids/liquids to the catalyst/epoxide mixture. To use PPN cocatalysts, the catalyst must first be pretreated by dissolving the catalyst and cocatalyst in a 4:1 benzene/methanol mixture followed by removing the solvent in vacuo overnight. Cr(salen) catalyst (50 mg) and cocatalyst were dissolved in 10 mL of neat epoxide. The solution was added via injection port into a predried 300 mL Parr autoclave maintained at 80 °C. The flask was then washed with another 10 mL of epoxide and added to the autoclave. The autoclave was charged with 55 bar CO_2 pressure and left at 80 °C. After a designated period of time, the autoclave was cooled to room temperature and vented in a fume hood. The copolymer was extracted as a dichloromethane solution and dried under vacuum at 100 °C. The isolated polycarbonate was weighed to determine turnovers and analyzed by ^1H NMR to determine the percent cyclic carbonate, polycarbonate, and polyether. *We have typically reported isolated copolymer yields for calculating TON and TOF's in our studies that are intrinsically lower than yields determined by ^1H NMR integrations.* In this regard it is important to note that in situ infrared spectroscopy monitoring of the formation of both copolymer and cyclic carbonate provides the same relative reactivities as a function of CO_2

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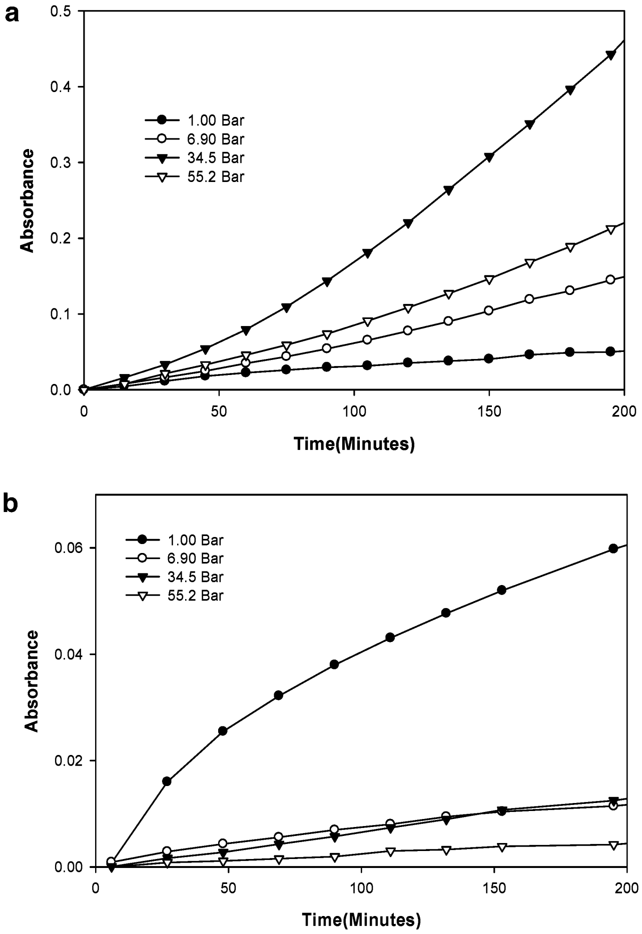

Figure 5. (a) Effect of CO_2 pressure on the rate of polycarbonate formation from the coupling of CO_2 and cyclohexene oxide using catalyst **1** and 3 equiv of tricyclohexylphosphine as a cocatalyst at 80 °C. (b) Effect of CO_2 pressure on the rate of cyclic carbonate formation from the coupling of CO_2 and cyclohexene oxide using catalyst **1** and 3 equiv of tricyclohexylphosphine as a cocatalyst at 80 °C.

pressure. For example, Figure 5 displays data obtained via ATR spectroscopy for the processes described in Table 2. Molecular weight determinations (M_w and M_n) were carried out at the New Jersey Center for Biomaterials, Rutgers University.

X-ray Structural Study. Crystals were grown from slow diffusion of pentane into a dichloromethane/tetrahydrofuran mixture. A Bausch and Lomb 10× microscope was used to identify suitable crystals from a representative sample of crystals from the same habit. The representative crystal was coated in paratone and fixed to a glass fiber fashioned to a copper mounting pin. The mounted crystals were then placed in a cold nitrogen stream (Oxford) maintained at 110 K on a Bruker SMART 1000 three-circle goniometer.[18]

The X-ray data were collected on a Bruker CCD diffractometer and covered more than a hemisphere of reciprocal space by a combination of three sets of exposures; each exposure set had a different φ angle for the crystal orientation, and each exposure covered 0.3° in ω. Crystal data and details on collection parameters are given in Table 4. The crystal-to-detector distance was 4.9 cm. Crystal decay was monitored by repeating the data collection for 50 initial frames at the end of the data set and analyzing the duplicate reflections; crystal decay was negligible. The space group was determined on the basis of systematic absences and intensity statistics.[19] The structure was solved by direct methods and refined by full matrix least-squares on F^2. All non-H atoms were refined with anisotropic displacement parameters. All H atoms attached to C atoms were placed in idealized positions and refined using a riding model with aromatic C−H = 0.96 Å, methyl C−H = 0.98 Å, and with fixed isotropic displacement parameters equal to 1.2 (1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they were attached. The methyl groups were allowed to rotate about their local 3-fold axis during refinement. Data reduction was performed using SAINTPLUS (Bruker[19]); data was solved using SHELXS-86 (Sheldrick[20]) and refined using SHELXL-97 (Sheldrick[21]). Molecular graphics and preparation of material for publication were done with SHELXTL-Plus version 5.0 (Bruker[22]).

Table 4. Crystal Data and Structure Refinement for Complex 2·THF

empirical formula	$C_{35}H_{44}Cl_2CrN_5O_5$
fw	737.65
temperature	110(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2(1)/c$
unit cell dimens	$a = 12.660(3)$ Å
	$b = 9.193(2)$ Å, $\beta = 97.081(5)°$
	$c = 30.630(8)$
volume	3537.6(15) Å^3
Z	4
density(calcd)	1.385 Mg/m^3
absorp coeff	0.523 mm^{-1}
$F(000)$	1548
cryst size	0.35 × 0.35 × 0.35 mm^3
θ range for data collection	1.34 to 27.56°
index ranges	$-16 \le h \le 8$, $-11 \le k \le 11$,
	$-39 \le l \le 39$
no. of reflns collected	21 263
no. of indep reflns	7877 [R(int) = 0.1188]
completeness to $\theta = 27.56°$	96.4%
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	7877/0/440
goodness-of-fit on F^2	0.994
final R indices [$I > 2\sigma(I)$]	R1 = 0.1028, wR2 = 0.2231
R indices (all data)	R1 = 0.2130, wR2 = 0.2776
largest diff peak and hole	0.558 and −0.522 e·Å^{-3}

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Supporting Information Available: Complete details for the crystallographic study of compound **2**·THF. This material is available free of change on the Internet at http://pubs.acs.org.

OM049454L

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(18) *SMART 1000 CCD*; Bruker Analytical X-Ray Systems: Madison, WI, 1999.

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

(20) Sheldrick, G. *SHELXS-86: Program for Crystal Structure Solution*; Institut fur Anorganische Chemie der Universitat: Gottingen, Germany, 1986.

(21) Sheldrick, G. *SHELXL-97: Program for Crystal Structure Refinement*; Institut fur Anorganische Chemie der Universitat: Gottingen, Germany, 1997.

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