Copolymerization of Carbon Dioxide and Cyclohexene Oxide Catalyzed by Chromium Complexes Bearing Semirigid [ONSO]-Type Ligands

Bing Han,[1] Li Zhang,[1] Samuel J. Kyran,[2] Binyuan Liu,[1] Zhongyu Duan,[1] Donald J. Darensbourg[2]

[1]School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, China
[2]Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77843
Correspondence to: B. Liu (E-mail: Byliu@Hebut.Edu.Cn) or D. J. Darensbourg (E-mail: Djdarens@Chem.Tamu.Edu)

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ABSTRACT: Chromium complexes supported by tetradentate dianionic imine-thioether-bridged bis(phenol) ligands were prepared and employed in the synthesis of poly(cyclohexene carbonate) via the copolymerization of CO_2 and cyclohexene oxide. The catalytic activity, product selectivity, and kinetic behaviors of these [ONSO]Cr^{III} complexes have been systematically investigated. Results indicate the presence of electron-withdrawing substituents on the ligands to enhance catalytic activity and polymer selectivity. A turnover frequency of 100 h^{-1} is observed at a temperature of 110 °C, producing polycarbonate with >60% selectivity. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 1938–1944

KEYWORDS: carbon dioxide; catalysts; copolymerization; polycarbonates; semirigid ligands

INTRODUCTION The alternative and greener approach to produce polycarbonates by the copolymerization of CO_2 with epoxides is of considerable interest as CO_2 utilization as a chemical feedstock is complementary to carbon capture and storage.[1] Since the pioneering work of Inoue et al. with $ZnEt_2/H_2O$ for CO_2 and propylene oxide copolymerization in 1969,[2] numerous homogeneous catalysts with magnesium, titanium, chromium, iron, cobalt, and zinc metal centers stabilized by various ancillary ligands such as porphyrin,[3] phenoxides,[4] β-diiminates,[5] β-ketoiminates,[6] salen/salalen/salan,[7–9] anilido-aldiminates,[10] and many others[11] have been explored to promote this process. These single-site metal catalysts with well-defined structures are active under mild reaction conditions and can also afford regio- and/or stereoselective copolymers with select ligand scaffolds.[3(c),5(e),7(b),7(c),12] Prominently employed are the [ONNO]-type tetradentate dianionic ligands with Cr^{III} and Co^{III} centers as they provide remarkable activity for CO_2/epoxide copolymerization.[7–9] But upon screening all homogeneous metal catalysts to date, very few examples of ligands bearing soft Lewis base donors are found for this copolymerization process.[13] Recently, Duchateau and coworkers employed an aminophosphine chelate on a Cr^{III} complex to catalyze the production of poly(cyclohexene carbonate) (PCHC) from CO_2 and cyclohexene oxide (CHO). The catalyst, however, showed low activity (turnover frequency (TOF) $< 30\ h^{-1}$) and provided low molecular weight polymers ($M_n < 1800$ Da) containing detectable ether linkages ($\geq 6\%$).[13(a)] Capacchione and coworkers introduced a dinuclear Fe^{III} complex coordinated by a dithioether–triphenolate ligand for the coupling reaction of CO_2 with epoxides, but this complex produces cyclic carbonates exclusively.[13(b)]

In this work, we describe the preparation of Cr^{III} catalysts bearing tetradentate imine-thioether-bridged bis(phenolate) ligands (Fig. 1) and study their use in CO_2/CHO copolymerization. Within the literature, there are only a couple instances where similar [ONSO]-type ligands are used in catalysis, namely their Ti^{IV} and Zr^{IV} complexes in olefin polymerization and the ring-opening polymerization of lactides, respectively.[14,15] These [ONSO]-type ligands can be considered to be analogous to a salalen ligand where the saturated amine has been replaced with a softer sulfur donor atom. It is known via comparative studies that the (salalen)Cr^{III} and (salan)Cr^{III} complexes exhibit higher catalytic activities for the copolymerization process than their unsaturated (salen)Cr^{III} counterpart.[8(a),9] This is attributed to the cis-coordination modes adopted by the more flexible [ONNO] ligands as noted through single-crystal X-ray crystallography and in part to the lower electrophilicity at the metal center. The semirigidity of [ONSO] ligands also provides a cis-coordination mode as was observed in the structure of an [ONSO]$TiCl_2$ catalyst.[14] It is then reasonable to anticipate [ONSO]Cr^{III} complexes to prefer

Additional Supporting Information may be found in the online version of this article.

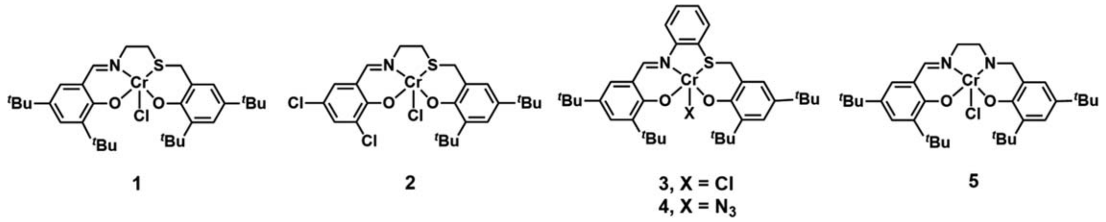


FIGURE 1 [ONSO]Cr^{III} catalysts employed in this study (**1–4**) and a (salalen)CrCl catalyst, **5** shown for comparison. Note: coordination geometries are not defined.

a cis-configuration as well and show favorable catalytic activity for CO_2/epoxide copolymerization. Further, the ease in preparation of various substituted derivatives of [ONSO] ligands, including those asymmetrical in nature will help modify the catalyst as desired. Thus, the catalytic behavior of [ONSO]Cr^{III} complexes is explored below with regards to its structure, activity, and the resulting copolymer selectivity.

EXPERIMENTAL

Materials and Methods

All manipulations of air- and moisture-sensitive compounds were carried out using standard Schlenk and vacuum line techniques under an argon atmosphere. Chromium(III) chloride tetrahydrofuran adduct ($CrCl_3·3THF$) was purchased from Strem Chemicals (98%). 3,5-Dichloro-2-hydroxybenzaldehyde (98%) was purchased from Tianjin Heowns Biochem Technologies. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde was purchased from Shanghai Haiqu Chemical industrial (98%). Bis(triphenylphosphine)iminium chloride ($[PPN]^+ = [Ph_3P\text{-}N{=}PPh_3]^+$) (PPNCl) (90%, Tianjin Heowns Biochem Technologies) was purified thrice by dissolving in acetone and precipitating by an excess amount of ether. The precipitate was dried under vacuum. Tetrabutylammonium chloride (TBACl) was recrystallized from ethanol prior to use. Cyclohexene oxide was refluxed over calcium hydride and distilled under a nitrogen atmosphere. Carbon dioxide (99.99% purity) was used without further purification. Toluene and tetrahydrofuran (THF) were refluxed and distilled from Na-benzophenone under dry nitrogen. Triethylamine was distilled over CaH_2. 2-Aminoethanethiol hydrochloride (98%), 2-aminothiophenol (99%), and *n*-butyllithium (*n*-BuLi) (2.5 M/L in hexane) were used without further purification. Bis(triphenylphosphine) iminium azide ($PPNN_3$) and 2-(bromomethyl)-4,6-di-*tert*-butylphenol were synthesized according to reported procedures.[16,17]

^1H and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer at frequencies of 400 MHz (^1H) and 100 MHz (^{13}C), respectively. All chemical shifts are provided in parts per million using tetramethylsilane as an internal reference at ambient temperature. IR spectra were obtained on a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} (16 scans collected). High-pressure reaction kinetic measurements were performed using an ASI React IR 1000 reaction analysis system with a stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor. UV–visible spectroscopy was performed in CH_2Cl_2 on a UV-CARY300 spectrometer. Molecular weight determinations were performed using a PL-GPC 220 instrument with a refractive index detector. The columns used were MIXED-B 300 × 7.5 mm columns held at 35 °C, using THF as eluent at a flow rate of 1.0 mL/min. ESI-MS were performed on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV and a spray current of 0.24 μA, capillary temperature 230 °C.

Synthesis of Ligand 1

A similar procedure to ligand **2** (see below) but using 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was carried out.

Yield: 78%. IR: 1627 cm^{-1}($\nu_{C=N}$), 1483 cm^{-1} (Ph ring $\nu_{C=C}$), 1272 cm^{-1} ($\nu_{Ar\text{-}O}$). UV–vis: 231, 263, 338 nm. ^1H NMR matches previously reported data:[15] (400 MHz, $CDCl_3$), $\delta = 8.31$ (*s*, 1H, NC*H*), 7.42 (*d*, 1H, Ar*H*), 7.27 (*d*, 1H, Ar*H*), 7.15 (*d*, 1H, Ar*H*), 6.95 (*d*, 1H, Ar*H*), 3.84 (*s*, 2H, ArC*H*$_2$S), 3.64 (*t*, 2H, C*H*$_2$), 2.72 (*t*, 2H, C*H*$_2$), and 1.27–1.43 ppm (*s*, 36H, C(C*H*$_3$)$_3$).

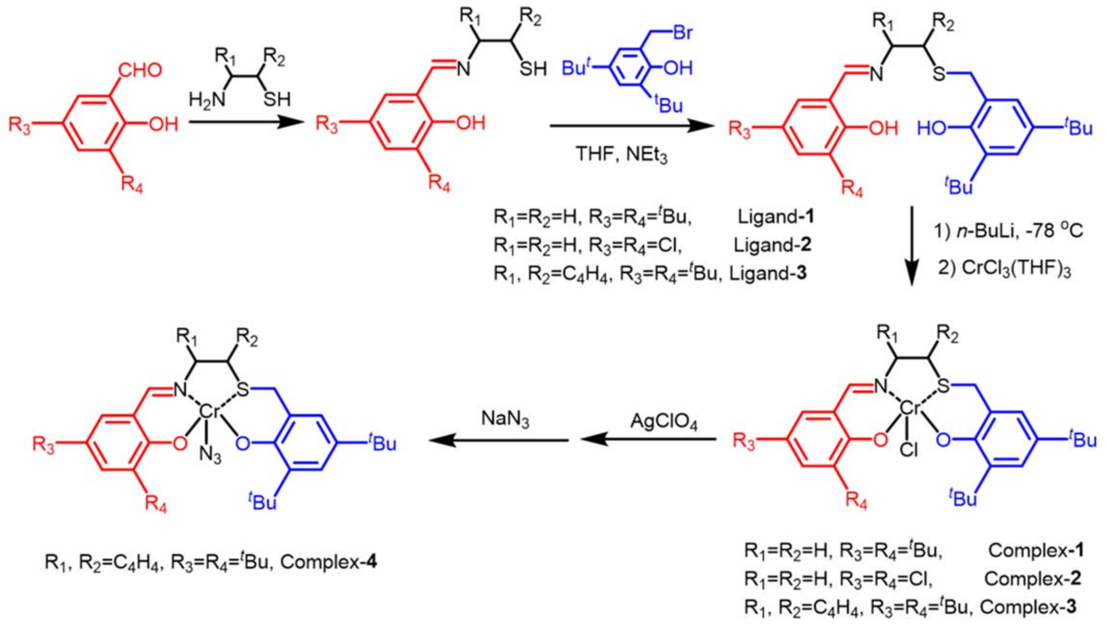
Synthesis of Ligand 2

A solution of 3,5-dichloro-2-hydroxybenzaldehyde (4.77 g, 25 mmol) in THF (20 mL) was added to a solution of triethylamine (2.51 g, 25 mmol) and cysteamine hydrochloride (2.27 g, 20 mmol) in THF (20 mL) and stirred 2 h at 20 °C. The reaction mixture was filtered under argon atmosphere and the filtrate was used for the next step without further purification. Triethylamine (2.51 g, 25 mmol) was added to the above filtrate, then a solution of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (5.94 g, 20 mmol) in THF (10 mL) was added dropwise over a period of 30 min. After the reaction was stirred for an additional 2 h, it was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexanes:EtOAc = 10:1) to afford the ligand **1** in yield of 65%.

IR: 1636 cm^{-1} ($\nu_{C=N}$), 1454 cm^{-1} (Ph ring $\nu_{C=C}$), 1287 cm^{-1} ($\nu_{Ar\text{-}O}$). UV–vis: 233, 264, and 338 nm. ^1H NMR (400 MHz, $CDCl_3$), $\delta = 8.19$ (*s*, 1H, NC*H*), 7.42 (*d*, 1H, Ar*H*), 7.28 (*d*, 1H, Ar*H*), 7.16 (*d*, 1H, Ar*H*), 6.93 (*d*, 1H, Ar*H*), 3.83 (*s*, 2H, ArC*H*$_2$S), 3.69 (*t*, 2H, CH_2), 2.75 (*t*, 2H, CH_2), and 1.28–1.41 (*s*, 18H, $C(CH_3)_3$), which is consistent with the reported data.[15]

Synthesis of Ligand 3

To a solution of 3,5-*di*-*tert*-butyl-2-hydroxybenzaldehyde (5.58 g, 25 mmol) in THF (20 mL) was added 2-aminothiophenol (2.50 g, 20 mmol), and the reaction mixture was refluxed for 2 h. Following this, triethylamine (2.51 g, 25



SCHEME 1 Preparation of ONSO donor ligands and their respective chromium(III) complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mmol) was added. After stirring for 15 min, a solution of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (5.94 g, 20 mmol) in dry THF (10 mL) was added dropwise over 0.5 h. The reaction mixture was refluxed for 4 h and filtered. The filtrate was evaporated under reduced pressure. Chromatography over silica gel eluting with hexanes-EtOAc (10:1) gave the target product as a yellow solid in a final yield of 74%.

IR: 1614 cm^{-1} ($\nu_{C=N}$). UV–vis: 234, 276, 363 nm. ^{1}H NMR (400MHz, $CDCl_3$), $\delta = 8.58$ (*s*, 1H, NC*H*), 7.48 (*d*, 1H, ArH), 7.36–7.45 (*d*, 1H, Ar*H*), 7.28 (*d*, 1H, Ar*H*), 7.22 (*d*, 1H, Ar*H*), 7.18 (*d*, 1H, Ar*H*), 7.14 (*d*, 1H, Ar*H*), 7.11 (*d*, 1H, Ar*H*), 6.82 (*d*, 1H, Ar*H*), 4.13 (*s*, 2H, ArCH_2S), and 1.20–1.49 ppm (*s*, 36H, $C(CH_3)_3$).

Preparation of Complexes 1–3

All complexes were synthesized using a modified procedure to that previously reported.[9(c)] *n*-BuLi (1.7 mL, 4.2 mmol) was added dropwise to a stirred solution of ligand (2.0 mmol) in THF (20 mL) at −78 °C. A color change from yellow to colorless is observed. The reaction mixture was allowed to warm to room temperature. After 0.5 h, the mixture was added to a flask containing $CrCl_3 \cdot 3THF$ (0.82 g, 2.2 mmol) and THF (10 mL) over a period of 30 min. Following an immediate color change of the chromium starting material from purple to dark green, the reaction mixture was stirred 24 h at 20 °C. The solvent was removed *in vacuo*, and the resulting solid was redissolved in dichloromethane. The reaction mixture was filtered to remove LiCl, and the solvent removed *in vacuo* to afford dark green complexes **1–3**.

Complex 1

Yield: 90%. IR: 1616 cm^{-1} ($\nu_{C=N}$),1458 cm^{-1} (Ph ring $\nu_{C=C}$), 1264 cm^{-1} ($\nu_{Ar\text{-}O}$). UV–vis: 230, 261, and 421 nm (weak). ESI-MS (*m*/*z*): [M+K+THF]$^+$: 708.36, Found 710.20

Complex 2

Yield: 92%. IR: 1623 cm^{-1} ($\nu_{C=N}$), 1437 cm^{-1} (Ph ring $\nu_{C=C}$), 1262 cm^{-1} ($\nu_{Ar\text{-}O}$). UV–vis: 232, 281, and 405 nm (weak). ESI-MS (*m*/*z*): [M+K+THF]$^+$ 663.15, Found 665.87

Complex 3

Yield: 95%. IR: 1611 cm^{-1} ($\nu_{C=N}$), 1470 cm^{-1} (Ph ring $\nu_{C=C}$), 1273 cm^{-1} ($\nu_{Ar\text{-}O}$). UV–vis: 233, 333, and 475 nm (weak). ESI-MS (*m*/*z*): [M+K+THF]$^+$: 755.35, Found 757.13

Preparation of Complex-4[9(c)]

$AgClO_4$ (0.07 g, 3.3 mmol) was added to an acetonitrile solution of Complex **3** (0.22 g, 3.3 mmol) and stirred for 24 h. The reaction mixture was then filtered and NaN_3 (0.64 g, 9.9 mmol) was added under argon. The reaction was allowed to stir for an additional 24 h. The solvent was removed *in vacuo*, and the resulting solid was redissolved in diethyl ether. The mixture was filtered and solvent was removed *in vacuo* yielding a dark brown powder in 60% yield. IR: 1611 cm^{-1} ($\nu_{C=N}$), 2094 cm^{-1} (ν_{N3}), 1477 cm^{-1} (Ph ring $\nu_{C=C}$), 1273 cm^{-1} ($\nu_{Ar\text{-}O}$). UV–vis: 229, 317, and 467 nm (weak). ESI-MS (*m*/*z*): [M+K+THF]$^+$: 762.39, Found 758.13.

General Method for Copolymerization of CO_2 and CHO

The copolymerization reactions were carried out in a 100-mL stainless-steel autoclave equipped with a magnetic stirrer which had been previously dried at 60 °C for 2 h under vacuum. In a typical experiment, the reactor is charged with the appropriate amount of catalyst and epoxide and pressurized with CO_2 to the desired pressure. The mixture is then heated to the temperature of interest while stirring at about 200 rpm for an expected time. The reactor is then cooled to ambient temperature, and the pressure slowly released. The crude mixture is treated with CH_2Cl_2 and stirred to give a homogeneous solution. A small sample of the CH_2Cl_2 solution is used for IR measurement to determine selectivity of PCHC and CHC. The residual mixture is condensed by rotary evaporation and treated with methanol. The resulting precipitate is filtered and purified twice more by the CH_2Cl_2/methanol workup. The final isolated solid is dried at 45 °C under vacuum overnight. The polymer was subjected to NMR analysis.

TABLE 1 Copolymerization of CO_2 and CHO with Complex **3** and Various Cocatalysts[a]

Entry	Cocatalyst (Equiv. to Cr)	TOF (h^{-1})[b]	Conv. (%)[c]	% PCHC[d]
1	$PPNN_3$ (2)	69	54	77
2	PPNCl (2)	67	57	72
3	PPNCl (1)	58	40	87
4	TBACl (2)	34	29	71
5	TBACl (1)	30	20	90

[a] Reaction conditions: CHO/catalyst = 1000/1, Complex **3**: 0.065 g (0.1 mmol), 3.0 MPa, 80 °C, 6 h.
[b] Turnover frequency as moles of CHO consumed per mole of catalyst per hour.
[c] Based on isolated yield of polymer and in conjunction with IR data.
[d] Selectivity of poly(cyclohexene carbonate), PCHC determined by IR spectroscopy: $A_{1745}/(A_{1745}+A_{1802})$.

TABLE 2 Effect of [ONSO]CrX Complexes on CO_2/CHO Copolymerization[a]

Entry	Cat./Cocat.	TOF (h^{-1})[b]	Conv. (%)[c]	% PCHC[d]	M_n (g/mol)[e]	PDI[e]
1	**1**/PPNCl	49	43	69	7,200	1.25
2	**2**/PPNCl	54	44	74	8,300	1.23
3	**3**/PPNCl	67	57	72	10,900	1.28
4	**3**/$PPNN_3$	69	54	77	–	–
5	**4**/PPNCl	68	55	75	9,900	1.25
6	**4**/$PPNN_3$	71	53	81	–	–

[a] Reaction conditions: CHO/catalyst/cocatalyst = 1000/1/2; 3.0 MPa, 80 °C, 6 h; CHO: 9.8 g (100 mmol).
[b] Turnover frequency as moles of CHO consumed per mole of catalyst per hour.
[c] Based on isolated yield of polymer and in conjunction with IR data.
[d] Selectivity of PCHC determined by IR spectroscopy: $A_{1745}/(A_{1745}+A_{1802})$.
[e] Polydispersity index (PDI) was determined by GPC.

RESULTS AND DISCUSSION

Condensation of various 2-hydroxybenzaldehydes with aminothiols provides the respective imine-thiol phenol compounds. Substitution of bromine in 2-bromomethylphenols by the thiol group in the presence of a base yields the desired bis(phenol) [ONSO] ligands (Scheme 1). Subsequent treatment with *n*-BuLi and an equivalence of $CrCl_3(THF)_3$ then generates the desired dark green [ONSO]CrCl complexes **1-3** in high yields. Complex **4** can be obtained from the reactions of Complex **3** with $AgClO_4$ and NaN_3 and is similar to the synthetic route employed for (salan)CrN_3.[9(c)] The paramagnetism of Cr^{III} precludes reliable NMR data but the complexes have been characterized via ESI-MS, IR, and UV–vis spectroscopies. The mass spectral data show the appropriate mass peaks of each complexes but with an added THF solvent molecule, that is, [ONSO]CrX·THF. Infrared analyses reveal the stretching frequency of C=N bond to have shifted to lower wavenumbers upon coordination of the ligand to the metal. In the electronic spectra, while the free ligands exhibit three absorption bands between 200 and 400 nm, the complexes display newer and weaker transitions including in the 400-500 nm range which are assigned to the ligand-to-metal charge transfers (Supporting Information Fig. S1).

With the complexes at hand, we first looked at the effect of three onium salts as cocatalyst for CO_2/CHO copolymerization activity with Complex **3** at 80 °C (Table 1). It was readily apparent that the bis(triphenylphosphine)iminium salts (PPNX) performed better, showing twice the catalytic activity than *n*-TBACl as seen in Entries 1–3 versus 4–5. This is due to the highly hygroscopic nature of TBACl which renders it difficult to isolate in a rigorously dry form unlike the PPNX salts. Thus, the presence of water lowers the activity via its competitive binding at the coordination site. Additionally, alkylammonium cations are more interactive with the anions than their bulky and delocalized PPN counterpart.[7(g),8(a)] Increasing the cocatalyst loading to two equivalents enhanced the TOFs (>60 h^{-1} with PPN salts) but dropped the copolymer selectivity below 80% (Entries 2 vs. 3; 4 vs. 5). These data indicate that, at higher loadings of the nucleophilic cocatalysts, the growing polycarbonate chain is more susceptible to being displaced from the metal center which can then backbite to produce the cyclic carbonate byproduct. While the use of azide versus chloride gave comparable activity, the selectivity for copolymer is slightly favored with the former as it is a poorer leaving group (Entries 1 vs. 2). On the other hand, a control reaction in the absence of a cocatalyst showed negligible activity with Catalyst **3** confirming that the active species must be a six-coordinate metal center derived from [ONSO]CrCl and a cocatalyst as has been

TABLE 3 Activity and Selectivity of PCHC Production with [ONSO]CrCl, 1 versus (salalen)CrCl, **5**

Entry	Cat./Cocat.	Loading[a]	*P* (MPa)	Time (h)	Temperature (°C)	TOF (h^{-1})	% PCHC
1	**1**/PPNCl	1,000/1/1	1.3	3	70	31	87
2[b]	**5**/PPNCl	1,000/1/1	1.3	3	70	51	100

[a] Loading ratio depicts CHO/catalyst/cocatalyst.
[b] Data obtained from Ref. 8(a).

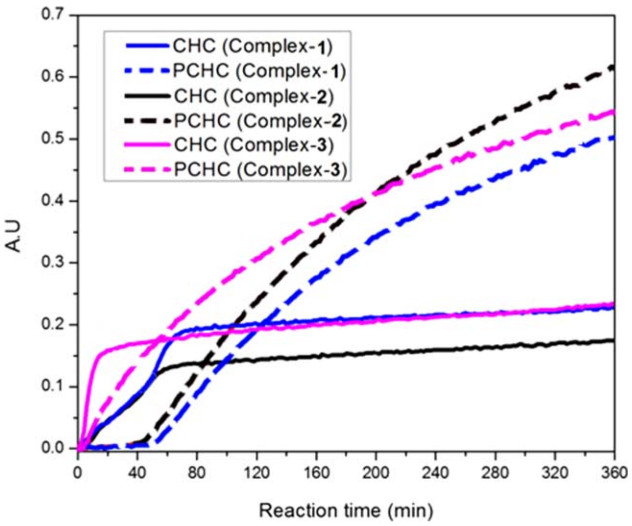


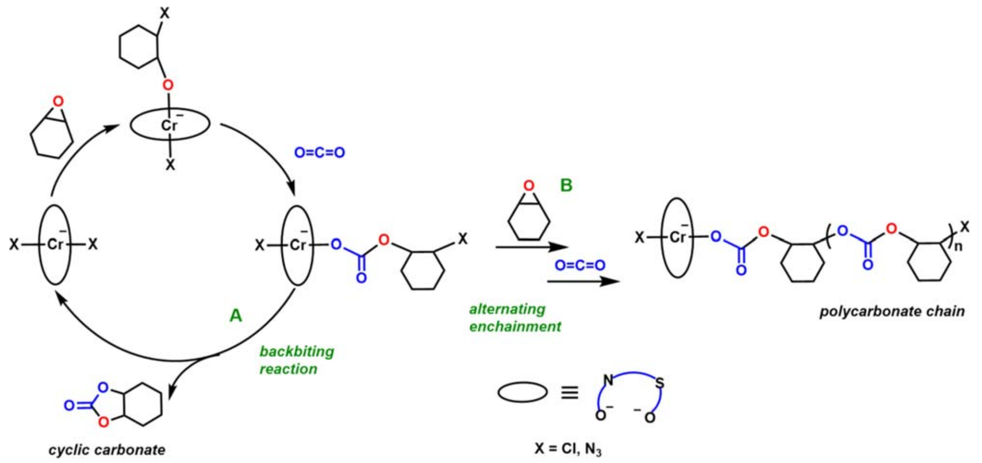
FIGURE 2 Absorbance versus time profiles of poly(cyclohexene carbonate) (PCHC) and cyclohexene carbonate (CHC) with [ONSO]CrCl complexes (**1–3**). Reaction conditions: [CHO]/catalyst/cocatalyst = 1400/1/2, 3.4 MPa, 80 °C. Dashed and continuous lines represent PCHC and CHC, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

established before.[7(g,h),8(a)] This can also be noted through infrared analysis on a mixture of $PPNN_3$ and Complex **3**. The metal-coordinated azide stretching frequency (2054 cm^{-1}) rather than the free azide band (2003 cm^{-1}) is observed (Supporting Information Fig. S2).[18,19]

When the catalytic activity was assessed for the [ONSO]Cr^{III} complexes (**1–3**), it was found that the better catalysts bore electron-withdrawing substituents on their ligands (Table 2). Thus, Catalyst **2** bearing two chlorides on a phenolate rather than *tert*-butyls and Catalyst **3** bearing a phenylene backbone instead of an ethylene linker display higher TOFs in comparison to Catalyst **1** (Entries 1–3). With the inductive withdrawing effect of phenylene felt directly by the N and S donor atoms, Catalyst **3** outperforms **2** (TOF of 67 vs. 54 h^{-1}) where the effect of chlorides from at least three bonds away are presumably less felt by the phenolate O donor. Catalyst **4** bearing an azide X ligand, versus X = Cl of **3**, displays nearly identical activity when it is employed with PPNCl to the reaction observed with **3**/$PPNN_3$ (Entries 4 and 5). This is as expected for they both essentially result in the same mixture of active species, that is, {[ONSO]Cr(Cl)(N_3)}PPN and the scrambled complexes, {[ONSO]CrX_2}PPN where X = Cl or N_3. Polymer selectivity is slightly enhanced with the use of azides (Entries 3–6) for reasons previously noted above in Table 1.

A comparison of Catalyst **1** with its salalen analog **5** shows the [ONSO]CrCl complex to be less active (TOF of 31 h^{-1} vs 51 h^{-1}) and produce more cyclic carbonate (>10%) when hardly any is observed with the (salalen)CrCl under identical conditions shown in Table 3. The poorer polymer selectivity can be attributed to a weaker interaction of the growing anionic polymer chain with a more electron-rich Cr^{III} center arising from the more electron-releasing sulfur donor. This then leads to a higher propensity for the polycarbonate to backbite on itself and yield the cyclic carbonate. It would also explain why electron-withdrawing substituents on the [ONSO] ligands help enhance the activity and selectivity for producing PCHC.

To further assess the influence of the structural features of [ONSO]CrCl Complexes (**1**–**3**) on the copolymerization process, reactions were monitored via *in situ* infrared spectroscopy by following the carbonate absorption intensities of polycarbonate (1750 cm^{-1}) and cyclic carbonate (1804 cm^{-1}) products. The reaction profiles are shown in Figure 2. Little to no induction periods and rapid formation of cyclic carbonate in the initial stages of the reaction (0–1 h) after which their growth is nearly suppressed is noted for all catalysts. Copolymer formation is only observed close to 50 min into the reaction with Catalysts **1** and **2**; about the same time, they display a significant rate drop in cyclic carbonate production. On the other hand, the least electron-rich Cr^{III} catalyst, **3**, favors polycarbonate production right from the start. Over a prolonged reaction time, the rate of copolymerization appears to be fastest



SCHEME 2 Proposed mechanism for the production of cyclohexene carbonate, Path A and poly(cyclohexene carbonate), Path B. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 4 Copolymerization of CO_2 and CHO with Catalyst **3** under Various Conditions[a]

Entry	CHO/**3**/PPNCl	Temperature (°C)	P (MPa)	TOF (h^{-1})[b]	% PCHC[c]
1	1,000/1/2	70	3.0	31	76
2	1,000/1/2	80	3.0	67	72
3	1,000/1/2	90	3.0	95	70
4	1,000/1/2	100	3.0	96	66
5	1,000/1/2	110	3.0	100	64
6	1,000/1/2	80	3.5	67	71
7	1,000/1/2	80	1.0	56	75
8	1,000/1/2	80	0.5	42	73
9	1,500/1/2	80	3.0	54	71
10	2,000/1/2	80	3.0	33	70

[a] Reactions were carried out over a period of 6 h.

[b] Turnover frequency as moles of CHO consumed per mole of catalyst per hour.

[c] Selectivity of PCHC determined by IR spectroscopy: $A_{1745}/(A_{1745}+A_{1802})$.

for **2**. From these observations, we have summarized a possible mechanism in Scheme 2. The reactions with [ONSO]Cr^{III} complexes are initially dominated by the backbiting process of a one-mer unit which leads to the cyclohexene carbonate (CHC) product, Path A. However, once enchainment of the monomer unit begins, backbiting to displace an alkyl carbonate is a lot less favored and the propagation of polymer chain is preferred (Path B). Similar findings are also seen with (salen)AlCl catalysts and porphyrin chromium complexes.[3,20(e)]

The NMR data of purified PCHC show the copolymer to be atactic in nature and display no polyether linkages with >99% CO_2 incorporation (Supporting Information Fig. S3 and S4). Bimodal molecular weight distribution is observed in GPC due to the presence of adventitious water which acts as a chain-transfer agent (Supporting Information Fig. S5).[7(l),11(e),20(a)] Number average molecular weights up to 11,000 Daltons are observed with narrow PDIs around 1.2 (Table 2). The influence of reaction temperature, pressure and the catalyst loading of **3** were also investigated for the copolymerization reaction and the results are summarized in Table 4. A rise in temperature from 70 to 110 °C drops polymer selectivity from 76 to 64% but more than triples the catalytic activity with TOF rising from 31 to 100 h^{-1} (Entries 1–5). Perfectly alternating copolymer is observed even at a pressure of 0.5 MPa (Supporting Information Fig. S6), but the catalytic activity drops by a third (Entries 2 and 6–8). Reducing catalyst loading from 0.1 to 0.05% reduces monomer conversion and thus subsequently the TOFs but maintains similar polymer selectivity (Entries 2 and 9–10).

CONCLUSIONS

To summarize our findings above, we have prepared a series of [ONSO]-type Cr^{III} complexes derived from semirigid imine-thioether-bridged bis(phenol) ligands. Analogous to (salalen)Cr^{III} complexes by bearing a more electron-releasing S donor versus a saturated N donor, these [ONSO]Cr^{III} catalysts show moderate activity and polycarbonate selectivity in comparison. The lower electrophilicity at the metal center disfavors the growth of anionic polymer chain in the initial stages of the reaction and tends to produce cyclic carbonates. The severity of the backbiting process to produce the byproduct can be lessened by introducing electron-withdrawing groups on to the ligands, which additionally increases the catalytic activity as well.

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