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Influence of the Metal (Al, Cr, and Co) and Substituents of the Porphyrin in Controlling Reactions Involved in Copolymerization of Propylene Oxide and Carbon Dioxide by Porphyrin Metal(III) Complexes. 3. Cobalt Chemistry

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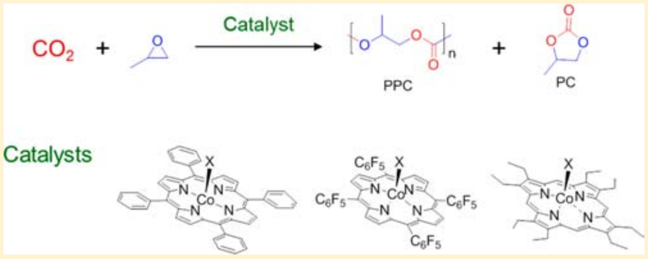
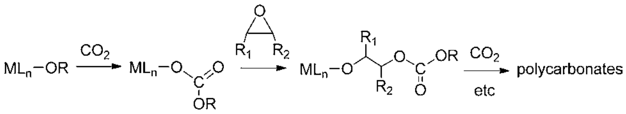
Supporting Information



ABSTRACT: A series of cobalt(III) complexes LCoX, where L = 5,10,15,20-tetraphenylporphyrin (TPP), 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TFPP), and 2,3,7,8,12,13,17,18-octaethylporphyirn (OEP) and X = Cl or acetate, has been investigated for homopolymerization of propylene oxide (PO) and copolymerization of PO and CO_2 to yield polypropylene oxide (PPO) and polypropylene carbonate (PPC) or propylene carbonate (PC), respectively. These reactions were carried out both with and without the presence of a cocatalyst, namely, 4-dimethylaminopyridine (DMAP) or PPN^+Cl^- (bis(triphenylphosphine)iminium chloride). The PO/CO_2 copolymerization process is notably faster than PO homopolymerization. With ionic PPN^+Cl^- cocatalyst the TPPCoOAc catalyst system grows two chains per Co center and the presence of excess $[Cl^-]$ facilitates formation of PC by two different backbiting mechanisms during copolymerization. Formation of PPC is dependent on both $[Cl^-]$ and the CO_2 pressure employed (1−50 bar). TPPCoCl and PO react to form TPPCo(II) and $ClCH_2CH(Me)OH$, while with DMAP, TPPCoCl yields $TPPCo(DMAP)_2{}^+Cl^-$. The reactions and their polymers and other products have been monitored by various methods including react-IR, FT-IR, GPC, ESI, MALDI TOF, EXAFS, and NMR (^1H, $^{13}C\{^1H\}$) spectroscopy. Notable differences are seen in these reactions with previous studies of (porphyrin)M(III) complexes (M = Al, Cr) and of the (salen)M(III) complexes where M = Cr, Co.

INTRODUCTION

Use of CO_2 in the production of polycarbonates, as shown in eq 1, in contrast to the use of diphenylcarbonate, phosgene, or one of its derivatives,[1] is an attractive alternative based on atom efficiency, cost, and environmental considerations.

1.


There are now many reports and some excellent reviews dealing with the use of coordination metal complexes that will catalytically combine CO_2 and epoxides to the respective cyclic carbonate or the polycarbonate.[2−9] Reactions involving CO_2 and propylene oxide (PO) are particularly sensitive to the nature of the metal and reaction conditions. As shown in Scheme 1 there are three competing pathways leading to polypropylene oxide (PPO), the cyclic carbonate, propylene carbonate (PC), and the polymer, polypropylene carbonate (PPC). In reactions A and B, PC is the thermodynamic product and thus PPC must be formed under kinetic conditions.[10] This provides quite a challenge to the chemist since backbiting reactions such as those depicted in Scheme 2 can lead to formation of PC by degradation of a PPC chain.

In addition, in considering the reactions shown in Scheme 1, we note that insertion of CO_2 into the alkoxide bond must occur efficiently; furthermore, since this is typically a reversible reaction the metal−alkylcarbonate must be kinetically more reactive than the metal−alkoxide bond in ring opening or enchaining the epoxide for PPC formation.

Despite these rather stringent requirements, catalytic PPC formation has been achieved with turnover frequencies (TOFs) of ~10^3 h^{-1}.[11−17] In addition, in the ring opening of PO by the carbonate this has been achieved with both regio- and stereoselectivity.[5,6] $^{13}C\{^1H\}$ NMR spectroscopy of the carbonate signal is typically employed in determination of

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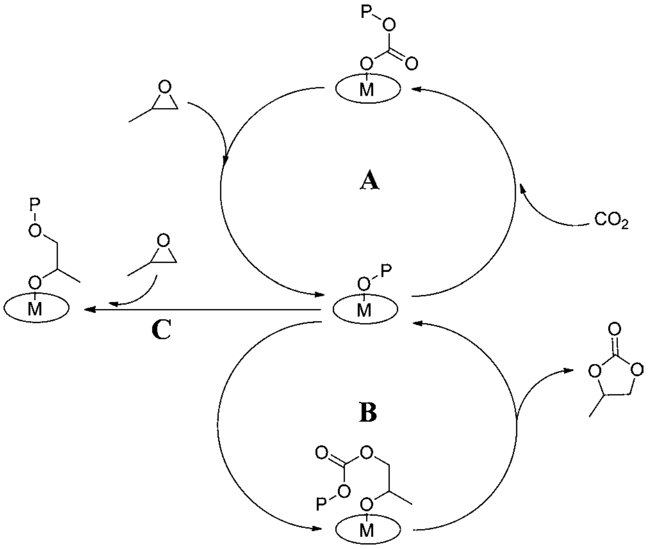
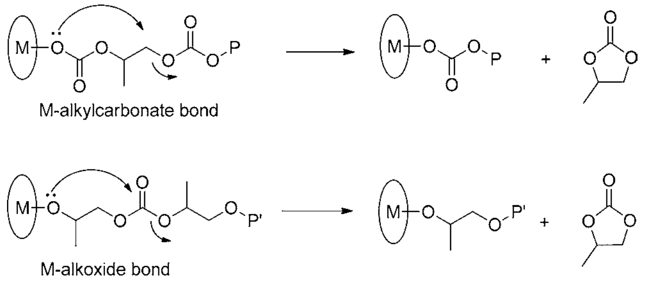
Scheme 1. Competing Reactions, A, B, and C Involved in the PO/CO_2 Copolymerization Processes[a]



[a] A yields PPC, B yields PC, and C yields PPO.

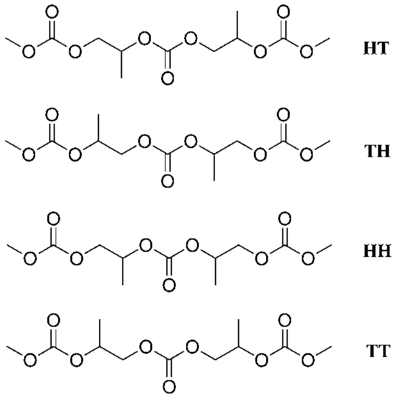
Scheme 2. Possible Backbiting Reactions To Produce PC[a]



[a] P and P′ represent growing polymer chains.

PPC microstructure at the triad sensitivity level. See Chart 1 for the regiosequences.

Chart 1. Possible Regiosequences in PPC



To date of all the coordinate catalysts employed those involving the Schiff base salen ligands have been the most efficient, and of these cobalt(III) has been the best with chromium(III) in second place.[5,15,16,18]

The first report of the copolymerization of CO_2 and PO by a trivalent metal was by Inoue, who employed tetraphenylporphyrin aluminum chloride as an initiator, TPPAlCl.[19,20] This was a very poor catalyst system in terms of TOFs. (Salen)AlCl, however, has been shown to be active in this coupling of PO and CO_2 to give PC but not PPC.[21−23]

We were attracted to use of the planar porphyrin ligands and wished to compare the reactivity of the trivalent metal complexes LMX, where L is one of the porphyrins shown in Figure 1 and the metal, M, is either Al, Cr, or Co in order to address the question what makes one preferable over the other. In this paper we describe our studies of cobalt chemistry and make a comparison to our earlier work with aluminum and chromium.[24,25]

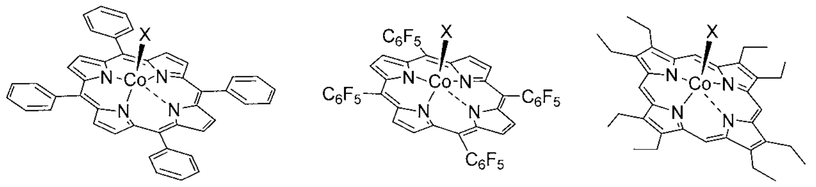
■ RESULTS AND DISCUSSION

Homopolymerization of PO. In the absence of a cocatalyst TPPCoCl and PO show little if any affinity toward either homopolymerization or in the presence of both PO and CO_2 to yield PC or PPC. However, a reaction between TPPCoCl and PO does occur leading to formation of TPPCo(II). Both TPPCoCl and TPPCo(II) are paramagnetic materials in solution, and the latter is notably less soluble in chlorinated solvents CH_2Cl_2 or $CHCl_3$ from which it precipitates as a fine powder. From this reaction we detected formation of the organic molecule 1-chloro-2-propanol ($HOCHMeCH_2Cl$), which is presumably formed by decomposition of the initially formed $TPPCoOCHMeCH_2Cl$. The related $TPPAlOCHMeCH_2Cl$ was previously identified in the reaction between TPPAlCl and PO in $CDCl_3$.[26] Interestingly, we found no evidence of formation of either an aldehyde or a ketone in these reactions. Either of these molecules should be easily detected by the presence of the strongly infrared active ν(C═O) group, but no such IR band was found in the product of the reaction between TPPCoCl and PO. Decomposition of a metal−alkoxide via β-hydrogen elimination is well documented,[27] and we initially suspected that formation of Co(II) might have occurred by a kinetically labile TPPCoH.

When the reaction between TPPCoCl and PO was carried out in the presence of 1,3-cyclohexadiene, we observed formation of benzene by ^1H NMR spectroscopy. This suggests that formation of the alcohol may well occur in CH_2Cl_2 and $CHCl_3$ via a radical pathway in which the alkoxide radical abstracts a hydrogen atom from the solvent. Irrespective of the mechanism of this reaction it is readily apparent that $TPPCoOCHMeCH_2Cl$ is notably more susceptible to reduction than are the related chromium and aluminum analogs. Indeed, all our attempts to isolate the initially formed $TPPCoOCHMeCH_2Cl$ resulted in obtaining TPPCo(II) as determined by EXAFS, vide infra.

Even in the presence of added DMAP or PPN^+Cl^- the (porphyrin)CoCl systems fail to homopolymerize PO. Addition of PPN^+Cl^- leads to formation of the paramagnetic $PPN^+TPPCoCl_2^-$ species, while DMAP reacts to form a diamagnetic complex $TPPCo(DMAP)_2^+Cl^-$ in $CDCl_3$ or CD_2Cl_2. This is the sole product in the presence of two or more equivalents of DMAP, and the cation $TPPCo(DMAP)_2^+$ was characterized by EXAFS and ^1H NMR spectroscopy. With 1 equiv of DMAP the equilibria involving TPPCoCl and $TPPCo(DMAP)_2^+Cl^-$ are presumably present, along with TPPCoCl(DMAP), though the latter compound was not detected by ^1H NMR spectroscopy.

Rather interestingly TPPCoOAc in the presence of either DMAP or PPN^+Cl^- will homopolymerize *rac*-PO to give regioregular PPO with isotactic enrichment (see Figure SI 1,



5,10,15,20-Tetraphenylporphyrin (TPP)

5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (TFPP)

2,3,7,8,12,13,17,18-Octaethylporphyrin (OEP)

X = Cl, OAc

Figure 1. (porphyrin)Co(III) catalysts employed in this study.

Supporting Information). The reaction is notably slower than that of the chromium system, and of the three (porphyrin)Co(III) systems employed in this work TPP is the most active: TOFs observed are 4 h^{-1} for OEP, 1 h^{-1} for TFPP, and 24 h^{-1} for TPP systems. The activity is somewhat comparable to that of the TPPAl(III) system studied earlier. This finding indicates that the initially formed $TPPCoOCHMeCH_2OAc$ and the subsequent alkoxide attached to the cobalt center in the growing chain $TPPCoOCHMeCH_2OP$, where OP = $(OCHMeCH_2)_nOAc$, are less prone to decomposition with formation of Co(II) than the chloro−alkoxide $TPPCoOCHMeCH_2Cl$.

Although it is not necessarily fair to draw conclusions based on the chemistry of (porphyrin)CoCl, we are inclined to the view that certain (salen)CoX initiators may be prone to reduction to Co(II).[5,15,28] We note, for example, that Coates in his studies of the copolymerization of PO and CO_2 found that, under equivalent reaction conditions, certain Co−X initiators gave varying molecular weights of PPC and yet had very similar PDI values (PDI = polydispersity index).[16] A plausible explanation is that some were prone to early decomposition to inactive (salen)Co(II) in their reactions with PO.

Finally, we address the question of whether or not the TPPCo(III) system is capable of growing two chains in the presence of an anionic cocatalyst initiator.

When TPPCoOAc and PO are allowed to react in the presence of PPN^+Cl^- the molecular weight of the polymer decreases as the PPN^+Cl^- concentration is increased from 0.5 to 1.0 equiv in a manner expected for two growing chains (M_n = 4200 Da for 0.5 equiv and M_n = 3000 Da for 1.0 equiv of PPN^+Cl^-). In addition, in the polymerization of PO by TPPCoOAc we observe by ESI MS and FT-IR spectroscopy polymer chains terminated in acetate together with some OH end groups (see Figure SI 2, Supporting Information). The latter arise from adventitious H_2O. When to this living system PPN^+Cl^- is introduced we observe chloride end groups in addition to OAc and OH, as shown in Figure SI 3, Supporting Information, and a bimodal polymer molecular weight by GPC. These results parallel those we found for the TPPCr(III) system[25] and are consistent with proposals by Darensbourg and Lu and Coates and their respective co-workers who invoke two growing chains with (salen)Co(III) catalyst systems.[7,9,16]

Copolymerization of PO and CO_2. TPPCoCl in the presence of 1.0 equiv of PPN^+Cl^- does not provide an active system for formation of PPC. PC is formed along with some decomposition to Co(II). Formation of PC probably reflects the favorable backbiting of the $(TPP)CoO_2COCHMeCH_2Cl$ moiety with regeneration of the Co−Cl bond as noted elsewhere for related chromium and aluminum systems.[25,29] In addition, at higher temperatures, TPPCoCl, PO, and CO_2 (50 bar) react catalytically to form exclusively PC as noted by earlier co-workers.[30,31]

A high pressure of CO_2 (50 bar) favors PPC formation. Reactions employing TPPCoOAc, PO, and 0.5 equiv of DMAP, PPN^+Cl^-, or PPN^+OAc^- with CO_2 (50 bar) are active in formation of near regioregular PPC with HT junctions, see Figure 2. MALDI TOF spectroscopic analysis of the PPC is shown in Figure SI 4, Supporting Information. Interestingly, as the CO_2 pressure is reduced PC formation increases relative to PPC until at 1 atm CO_2 PC is predominantly formed.

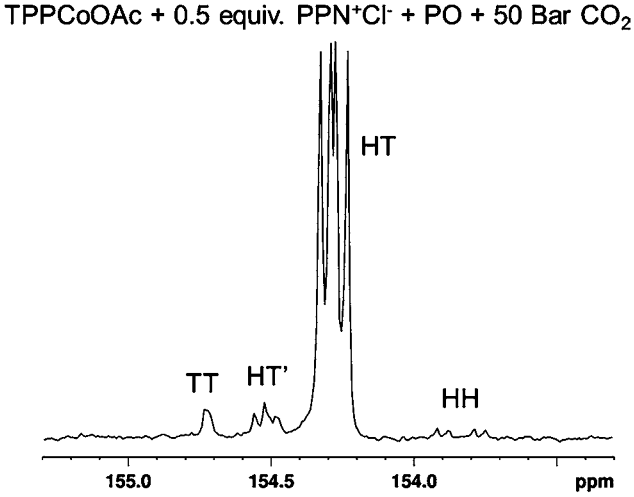


Figure 2. $^{13}C\{^1H\}$ of the carbonate in PPC showing near-perfect formation of the regio regular HT junction. HT′ has either an ether-rich carbonate or an end group.

In the chemistry of (salen)Co(III) complexes the need for relatively high pressures of CO_2 was noted early on by Coates and co-workers.[15,16] Our interpretation of these observations is that higher pressures of CO_2 are required to drive the equilibrium between the Co−alkoxide and the Co−alkylcarbonate in favor of the latter. Unless this equilibrium favors the alkylcarbonate the metal−alkoxide bond will be capable of enchaining PO to give ether-rich PPC or backbiting the PPC chain to give PC. Since the homopolymerization of PO is relatively slow for Co(III) systems we do not see ether-rich PPC but rather formation of PC. It is, however, also worth noting that cobalt is like aluminum in favoring the ring opening of PO by the alkylcarbonate bond relative to the cobalt−alkoxide bond.[24] This is in stark contrast to the chemistry of chromium(III) where enchainment of PO is [Cr]−OR > $[Cr]-O_2COR$.[25]

Comparative data for the three porphyrin systems are given in Table 1 along with some relative data for the chemistry of aluminum and chromium. Once again we see that TPP is the preferred porphyrin ligand, and the reactivity of the metals is in the order Cr > Co ≈ Al.

Table 1. TOFs Observed with (porphyrin)M(III)X Catalysts[a]

entry	catalysts	equiv of PPN^+Cl^-	TOF[b] (h^{-1})	% HT[c]	M_n[d]	PDI[d]
1	TPPCoCl	0.5	20	96	4900	1.30
2	TPPCoCl	1.0	28[e]			
3	TPPCoOAc	0.5	140	96	8500	1.30
4	OEPCoOAc	0.5	12	86	3100	1.20
5	TFPPCoOAc	0.5	4.8[e]			
6	TPPAlCl	0.5	73	75	12 000	1.30
7	TFPPAlCl	0.5	120	81	19 000	1.20
8	TPPCrCl	0.5	1600[f]		22 000, 8 100	1.10, 1.20
9	TPPCrCl	1.0	150	85	13 000	1.30

[a] Reaction conditions: 0.85 mL of PO (12 mmol.), 50 bar of CO_2, 0.02 mmol of catalyst, 0.01 mmol of additives when used, reaction time 5 h for entries 4 and 5 and 2.5 h for the rest, 25 °C. [b] Calculated from ^1H NMR analysis of reaction aliquots, TOFs calculated as (mmol of PO consumed)/(mmol of catalyst·reaction time). [c] Calculated from ^{13}C NMR spectra of pure polymers. [d] GPC analysis of pure copolymers after 100% PO consumption using polystyrene standard. Calculated maximum molecular weight 34.8 kDa (for 1 polymer chain growing per metal center). Observed lower molecular weights are attributed to chain transfer due to the presence of adventitious water. [e] PC was produced as the major product. [f] Ether-rich copolymer was produced along with a distinctly bimodal M_n distribution.

In the presence of >1.0 equiv of PPN^+Cl^-, PC formation competes with PPC, and at 5.0 equiv of PPN^+Cl^- only PC is formed. We also observed by in situ react IR spectroscopy that addition of PPN^+Cl^- to a living system growing PPC chains causes decomposition of PPC and formation of PC. This behavior is similar but somewhat slower than what we observe for chromium[25] and we believe is due to displacement of the carbonate-bound growing chain which facilitates backbiting. Similar proposals of Cl^--promoted chain transfer leading to PC formation have been invoked for (salen)Co(III) systems in their reactions with CO_2.[9,29,32]

EXAFS Studies. *TPPCo(II).* The sample examined was prepared from reaction between TPPCoCl and PO in the presence of 1.0 equiv of DMAP. Addition of PO to this catalyst system led to formation of TPPCo(II). The bond distance of the Co−N axial ligand was estimated to be 2.02 Å. The equatorial four Co−N bond distances in TPPCo(II) are 1.94 Å. No evidence of the Co−Cl bond was found. The axial Co−N could also be a Co−O since both scatter X-ray identically. The Co oxidation state was determined from the energy of the pre-edge peak and was 7.7085 keV, identical to that of Co(II) reference compounds; see the Experimental Section on EXAFS for the pre-edge energy position of Co(I), Co(II), and Co(III) reference compounds. EXAFS and XANES spectra of these reference compounds are shown in Figures SI 5 and 6, Supporting Information, and those of TPPCo(II) and TPPCo(III) samples are shown in Figures SI 7 and 8, Supporting Information.

$TPPCo(DMAP)_2{}^+Cl^-$. Microcrystalline sample was prepared from reaction between TPPCoCl and DMAP (2.5 equiv) in CH_2Cl_2. In this sample 2 axial Co−N bonds were observed, in addition to 4 Co−N bonds from the TPP. The Co−N region was fit to be 6 Co−N. Assuming that the 4 Co−N from the TPP do not change (XRD shows that the bonds are slightly larger when coordinated to an axial ligand) the bond distance of the 2 new axial Co−N was ∼2.04 Å or about 0.12 Å longer than the Co−N TPP bond distances. The energy of the Co K-edge XANES pre-edge was 7.7095 keV, consistent with Co(III) (see Figure SI 9, Supporting Information).

$TPPCo(H_2O)_2{}^+Cl^-$. We are not aware of any structure of a five-coordinate TPPCoCl, though $TPPCoCl(H_2O)$ is known where H_2O occupies the position trans to the Co−Cl bond. Given the preparation of TPPCoCl reported[33] and employed in this study it is likely that $TPPCoCl(H_2O)$ is the correct formation. We were not able to obtain single crystals of our porphyrin cobalt chloride suitable for single-crystal X-ray studies, so we again resorted to the use of EXAFS on a powdery microcrystalline sample (see Figure SI 8, Supporting Information). As we describe below, this sample did not prove to have a Co−Cl bond but rather was found to be Co(III) with four Co−N bonds in the equatorial plane assignable to the porphyrin ligand and two longer axial bonds which could be assignable to the light atoms O or N. The fit of all 6 Co−N bonds was 2.00 Å. Assuming that the 4 Co−N bonds from TPP remained unchanged, the axial Co−N bond distance was estimated to be 2.16 Å. Given the preparation and that analysis clearly was consistent with $TPPCoCl(H_2O)_x$ we believe that this sample contained the pseudo-octahedral $TPPCo(H_2O)_2{}^+$ cation, with a chloride counteranion. The presence of chloride was confirmed by elemental analysis (see Experimental Section for details).

Concluding Remarks. It is now possible to compare the reactivities of the three different metals under comparable conditions and offer some reasonable speculation concerning these intriguing reactions involving PO and CO_2 that can yield three different products as shown in Scheme 1.

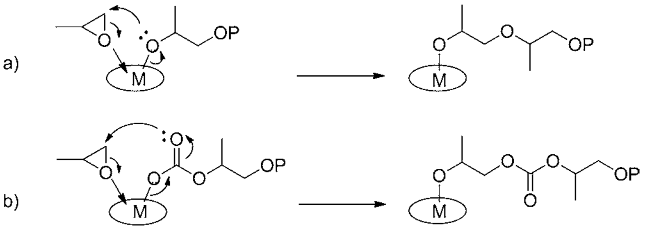
1. The role of the cocatalyst be it DMAP, PPN^+Cl^-, or imidazole, as was often employed in the early works of Inoue, can be understood in terms of activating the trans M−X bond. A good donor will lengthen the M−X bond and also by being a Lewis base increase the polarity of the M−X bond. This will enhance CO_2 insertion into the metal−alkoxide bond, as was nicely seen in the equilibrium involving $[Al]-OR + {}^{13}CO_2 = [Al]-O_2{}^{13}CR$ for the various porphyrins upon addition of DMAP.[24] The longer M−O bond in the six-coordinate complex will also allow the PO molecule, which is to be enchained (ring opened), to more readily approach the metal center. It could also be argued that the *trans* effect promotes dissociation of the alkylcarbonate. We find no evidence for free polycarbonate chains during formation of PPC as our evidence involving Cl^- displacement favors formation of PC by backbiting. We do note, however, that Darensbourg and Lu and co-workers found a tetrahedral quaternarized HN^+ group which was bound to the salen ligand attached to Co(III) further labilized the alkylcarbonate by $N^+-H\cdots O$ carbonate bonding.[7,9] This hydrogen bonding would lengthen the Co−O bond of the carbonate and thus facilitate PO activation at the electrophilic Co(III) metal center.
2. In our earlier gas-phase studies of the binding of PO to the $TPPM^+$ centers[34] aluminum bound one PO molecule

the most strongly as determined by Ar atom bombardment. However, chromium and to a lesser extent cobalt-bound PO in a cooperative manner, thus favoring the six-coordinate $TPPM(PO)_2^+$ cation. This is not surprising. Aluminum with $z = 13$ is the cation with the least number of electrons to provide shielding of the positive charge, while both Cr(III) and Co(III) enjoy a significant ligand field stabilization for the six-coordinate pseudo-octahedral ion. We see this in this work with our characterization of $TPPCo(DMAP)_2^+$ and $TPPCo(H_2O)_2^+$. It is also surely this preference for six coordination that favors formation of two growing chains for Cr and Co but not for Al.

3. In comparing the ring opening of PO we see that the reactivity order is Cr > Al ≈ Co. We propose that this reflects the fact that the Cr−O bond has the greatest polarity $Cr^{\delta+}-O^{\delta+}$ for both the alkoxide and the alkylcarbonate. In comparing Cr(III) and Co(III), we note the well-accepted trend that as one proceeds from left to right across the d-block transition elements the electronegativity of the metals increase. [The group 11 metals, Cu, Ag, and Au, do not react with H^+ to give H_2.] Thus, Co(III) is a better oxidizing agent than Cr(III), as was elegantly demonstrated by Taube on the now classic example of inner-sphere electron transfer $Cr^{II} + Co^{III}-Cl \rightarrow Cr^{III}-Cl + Co^{II}$.[35] In this work we see the reduction of TPPCoCl to TPPCo in its reaction with PO. Similar formation of $TPPCr^{II}$ would be highly unlikely, and no reduction of the Cr(III) porphyrin complexes was observed in their reactions with PO.[25] In general, as one proceeds across the periodic table the electronegativity of the elements increases, and so while $Ti^{3+}(aq)$ is a reasonable reducing agent, $Fe^{3+}(aq)$ is a mild oxidizing agent. Similarly, for the lighter element aluminum the M(III)−O bond is likely to be less polar than that of Cr(III), and thus, aluminum and cobalt are rather similar in their reactivities. For both Cr and Co, the reactivity order is TPP > TFPP ~ OEP and the latter is virtually inactive, but for Al, the activity order is TFPP > TPP > OEP. This order appears to reflect upon the electrophilicity of the metal centers and in the absence of PPN^+Cl^- the TFPPMCl complexes where M = Al or Cr react with PO to give regioirregular PPO. The poorer reactivity of the OEP complexes probably arises from the poorer Lewis acidity of the metal centers. The interplay of these electronic effects is also seen in the recent report by Rieger and co-workers on the reactivity of para substituents on TPPCoCl with PO and CO_2.[36]

   In addition, in comparing the reactivity of Cr(III) and Co(III) we note that the d^6 ion is more likely to react via dissociative substitution when compared to the "half-filled t_{2g}"$-d^3$ ion. Since the reaction between the growing chain and PO occurs within the same hemisphere the uptake of PO at the metal center by an associative mechanism should be easier for Cr(III), which again would lead to its greater reactivity.
4. The reactivity order with respect to ring opening of PO, $M-O_2CR$ > M−OR for M = Al and Co, again emphasizes the similarity in these metals in this system. We speculate that this is due to the more covalent nature of the metal−alkoxide bond which leads to its low activity. The M−O bond in the alkyl carbonate will be longer, more polar, and more like a metal carboxylate than a metal alkoxide. Why this reactivity order is reversed for M = Cr is not clear, but it should be noted that the $Cr-O_2COR$ group still enchains PO faster than $M-O_2COR$ where M = Al and Co.
5. The reactivity of any metal center is greatly influenced by its attendant ligands in coordinate catalysis. Thus, it is not necessarily surprising to find that salen metal(III)-complexes for Cr(III) and Co(III) have similar reactivities in their reactions with CO_2 and epoxides with cobalt being slightly more reactive. This is clearly not so for the porphyrin systems.[37,36] Just why this is so is not clear.
6. The enchainment of PO in formation of PPO at a single metal center is in many ways similar to growth of a polyolefin chain in olefin polymerization.[38] The substrate, PO or alkene, is activated by coordination to an electrophilic metal center. The polar metal−alkyl or metal−alkoxide bond undergoes a 1,2-addition to the activated substrate to regenerate the metal−alkyl or metal−alkoxide bond. We can envisage the same for the metal−alkylcarbonate, though in addition to a 1,2-addition akin to the alkoxide, the alkylcarbonate could react via a six-membered transition state. These possibilities are shown in Scheme 3.

Scheme 3. Enchainment of Coordinated PO by (a) M−Alkoxide Bond and (b) M−Alkylcarbonate Bond[a]



[a] P and P′ represent growing polymer chains.

7. We note that at present no M(IV)- or M(I)-containing complexes have been reported to copolymerize epoxides and CO_2. We speculate that transition metals in the +4 oxidation state may have too covalent M−OR bonds, i.e., their bonds are not sufficiently polar, while M(+) metals may lack in electrophilicity and form M−μ-OR bonds where the oxygen lone pairs are otherwise engaged in interactions with the metal ions and are thus not available to attack the substrate. Only a limited number of main group and transition metal ions in the +2 and +3 oxidation states have been found to be active and for the latter only transition metals of the first row. We also note that for the M(2+) ions of zinc and magnesium only relatively low coordinate and binuclear metal complexes[39−42] have proved active where the larger, softer 5-coordinate Ca^{2+} in the complex $Tp^{but}Ca(OR)(PO)$ binds PO but does not ring open it.[43] This does not mean that Ca^{2+} ions cannot activate PO in ring opening as the early Union Carbide heterogeneous catalyst for formation of polyethylene oxide and PPO employed calcium.[44] Thus, aside from the obvious requirement of steric access to the metal center in order for substrate activation it appears that a rather specific charge/radius may be required for any M^{n+} ion, leading to activation of

PO along with an apparently polar adjacent metal—OR bond.

Hopefully the present findings described herein will not only contribute to the rapidly developing body of work on the copolymerization of epoxides and CO_2 by coordinate catalysis but will also stimulate further thought and research on these reactions which could become technologically transformative in production of polycarbonates by a greener, atom-efficient process involving utilization of CO_2.

EXPERIMENTAL SECTION

Reagents and Methods. All syntheses and solvent manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk-line and drybox techniques. Dimethylformamide was dried and distilled over calcium hydride and degassed before use. All other solvents were dried and degassed by standard methods. Deuterated solvents were stored over 4 Å molecular sieves for 24 h prior to use. Propylene oxide (Sigma Aldrich) was distilled from calcium hydride. All three porphyrins 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine ($TPPH_2$), 5,10,15,20-tetrakis(pentafluorophenyl)-21*H*,23*H*-porphine ($TFPPH_2$), and 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine ($OEPH_2$) (Frontier Scientific), anhydrous $CoCl_2$ (Aldrich), and 99% CO_2 (OSU gas stores) were used as received. Bis-(triphenylphosphine)iminium chloride($(Ph_3P)_2N^+Cl^-$) (Sigma Aldrich) was dried under vacuum and stored inside a drybox before use. 4-Dimethylaminopyridine (DMAP) (Aldrich) was sublimed and stored inside a drybox before use. PPN^+OAc^- was prepared from PPN^+Cl^- following a literature procedure.[45]

NMR Spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR experiments were carried out with a Bruker DPX-400 (5 mm broad band probe) and a Bruker DRX-500 (5 mm broad band probe) spectrometer. All chemical shifts are in ppm relative to the solvent chloroform-*d* at 7.24 ppm for ^1H NMR and 77.23 ppm for $^{13}C\{^1H\}$ NMR spectroscopy.

EXAFS Study. X-ray absorption spectroscopy data collection and analysis: Co K-edge (7.7090 keV) X-ray absorption measurements were conducted on the bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT, 10-ID) at the Advanced Photon Source (APS), Argonne National Laboratory. Ionization chambers were optimized for maximum current with linear response (ca. 10^{10} photons detected per second) using N_2 (10% absorption) in the incident X-ray detector and a mixture of ca. 30% Ar in N_2 (60% absorption) in the transmission X-ray detector. A third detector in the series simultaneously collected a Co foil reference spectrum with each measurement for energy calibration. The X-ray beam was 0.5 × 1.5 mm, and data was collected in transmission geometry in 10 min at step scan mode.

The energy of the pre-edge in the Co K-edge XANES was used to determine the oxidation state of the samples and calibrated from the position of standards $(ClCo(I)(PPh_3)_3$ (7.7081 keV), $Co(II)(Ac)_2 \cdot 2H_2O$ (7.7086 keV), $Co(II)(AcAc)_2 \cdot H_2O$ (7.7085 keV), $Co(II)Cl_2$ (7.7086 keV), $Co(II)F_2$ (7.7086 keV), $Co(III)(AcAc)_3$ (7.7094 keV), and $LiCoO_2$ (7.7093 keV) all obtained from Sigma-Aldrich). EXAFS fits were determined from experimental phase shift, and backscattering amplitudes were obtained from the $Co(NH_3)_6Cl_3$ (6 Co—N at 1.94 Å) and $ClCo(PPh_3)_3$ (1 Co—Cl at 2.25 and 3 Co—P at 2.33 Å; i.e., 4 Co-X at an average bond distance of 2.31 Å) for Co—Cl scattering. Standard procedures based on WINXAS 3.1 software were used to fit XAS data. EXAFS coordination parameters were obtained by a least-squares fit in q and r space of the first-shell nearest neighbor, k^2-weighted Fourier transform data.

Gel Permeation Chromatography. Gel permeation chromatographic (GPC) analyses were carried out at 40 °C using a Waters Breeze system equipped with a Waters 2414 refractive index detector and a set of two columns, Waters Styragel HR-2 and HR-4 (7.8 × 300 mm). THF was used as the mobile phase at 1.0 mL/min. Samples were filtered before analysis. Sample concentration was 1.0%, and injection volume was 100 μL. The calibration curve was made with three polystyrene standards covering the molecular weight range from 1320 to 3.15×10^6 Daltons.

Mass Spectrometry. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) was performed on a Bruker Microflex mass spectrometer provided by a grant from the Ohio BioProducts Innovation Center. The spectrometer was operated in a linear, positive ion mode with N_2 laser. Laser power was used at a threshold level required to generate a signal. The accelerating voltage was 28 kV. Equal amounts of the dithranol matrix and sample were dissolved in dichloromethane (approximately 2 mg/0.5 mL). A small amount of this solution was spotted on the target plate and allowed to dry at room temperature before use. Electrospray ionization mass spectroscopy (ESI MS) was carried out in positive ion mode on a Bruker MicrOTOF mass spectrometer provided by a grant from the Ohio BioProducts Innovation Center.

FTIR Spectroscopy. IR spectra were recorded in dichloromethane solution using a Perkin-Elmer Spectrum GX spectrometer at room temperature. For polymer samples films were prepared by slow evaporation of CH_2Cl_2 solution of the polymer on a circular NaCl plate of 2 mm thickness and 25 mm diameter. An ASI react-IR 1000 Reaction Analysis System was used to monitor the PO and CO_2 copolymerization reactions at atmospheric pressure of CO_2.

Microanalysis. Microanalysis was performed by Atlantic Microlab Inc

SQUID. Direct current magnetic susceptibility data were collected at the University of Florida using a Quantum Design MPMS-XL SQUID susceptometer equipped with a 7 T magnet and operating in the 1.8—300 K range. Magnetization versus field data were fit using the program MAGNET.[46] Both TPPCoCl and TPPCoOAc were found to be diamagnetic in the solid state, as shown in Figure SI 10, Supporting Information.

Synthesis of Catalysts. The series of (porphyrin)Co(III)X catalysts, where porphyrin = TPP, TFPP, OEP and X = chloride and acetate, were prepared according to previously reported procedures[31,47−49] and characterized by ^1H NMR, ESI-MS, and elemental analysis. Anal. Calcd for $TPPCoCl(H_2O)$: C, 72.88; H, 4.17; N, 7.73; Cl, 4.89. Found: C, 72.72; H, 4.10; N, 7.66; Cl, 5.15. Anal. Calcd for OEPCoOAc: C, 70.14; H, 7.28; N, 8.61. Found: C, 70.05; H, 7.38; N, 7.53. Anal. Calcd for TFPPCoOAc: C, 50.66; H, 1.02; N, 5.14. Found: C, 50.34; H, 0.89; N, 5.30.

$(TPP)Co(DMAP)_2{}^+Cl^-$. ^1H NMR ($CDCl_3$, δ, ppm): 0.25 (C*H*, doublet (DMAP)); 2.90 (CH_3, singlet (DMAP)); 4.05 (C*H*, doublet (DMAP)); 7.7 (12H, multiplet (phenyl)); 7.9 (8H, multiplet (phenyl)); 9.0 (8H, singlet (pyrrole)).

ASSOCIATED CONTENT

Ⓢ Supporting Information

$^{13}C\{^1H\}$ NMR, MALDI TOF MS, ESI MS and FT-IR spectra of polymers, EXAFS and SQUID data of the TPPCo(III) complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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