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Mechanistic Aspects of the Copolymerization of CO_2 with Epoxides Using a Thermally Stable Single-Site Cobalt(III) Catalyst

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Abstract: The mechanism of the copolymerization of CO_2 and epoxides to afford the corresponding polycarbonates catalyzed by a highly active and thermally stable cobalt(III) complex with 1,5,7-triabicyclo[4,4,0] dec-5-ene (designated as TBD, a sterically hindered organic base) anchored on the ligand framework has been studied by means of electrospray ionization mass spectrometry (ESI-MS) and Fourier transform infrared spectroscopy (FTIR). The single-site, cobalt-based catalyst exhibited excellent activity and selectivity for polymer formation during CO_2/propylene oxide (PO) copolymerization even at temperatures up to 100 °C and high [epoxide]/[catalyst] ratios, and/or low CO_2 pressures. The anchored TBD on the ligand framework plays an important role in maintaining thermal stability and high activity of the catalyst. ESI-MS and FTIR studies, in combination with some control experiments, confirmed the formation of the carboxylate intermediate with regard to the anchored TBD on the catalyst ligand framework. This analysis demonstrated that the formed carboxylate intermediate helped to stabilize the active Co(III) species against decomposition to inactive Co(II) by reversibly intramolecular Co−O bond formation and dissociation. Previous studies of binary catalyst systems based on Co(III)−Salen complexes did not address the role of these nucleophilic cocatalysts in stabilizing active Co(III) species during the copolymerization. The present study provides a new mechanistic understanding of these binary catalyst systems in which alternating chain-growth and dissociation of propagating carboxylate species derived from the nucleophilic axial anion and the nucleophilic cocatalyst take turns at both sides of the Co(III)−Salen center. This significantly increases the reaction rate and also helps to stabilize the active SalenCo(III) against decomposition to inactive SalenCo(II) even at low CO_2 pressures and/or relatively high temperatures.

Introduction

The catalytic transformation of carbon dioxide into biodegradable polycarbonates by the alternating copolymerization with epoxides[1] has attracted much attention in the last decades due to the economic and environmental benefits arising from the utilization of renewable source and the growing concern on the greenhouse effect. Numerous catalyst systems have been developed for this transformation.[2−7] Prominent among these are the binary or bifunctional catalyst systems based on cobalt−Salen complexes. These systems provides for efficient CO_2/epoxides coupling reactions even under mild conditions and in some cases allow for the regio- and/or stereoselective polymerization,[8−11] in which the enhanced glass transition temperature was observed in the resulting polycarbonates.[12] Prior to these studies of (salen)CoX catalysts, Coates and coworkers were the first to report the use of chiral SalcyCoX (salcy = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) complexes with a nucleophilic axial X group alone as catalysts for CO_2/propylene oxide (PO) copolymerization. This approach produced poly(propylene carbonate) (PPC) with >99% selectivity and with 90−99% carbonate linkages at a CO_2 pressure of 55 bar and ambient temperature.[13]

Although simple SalenCo(III)X complexes alone could catalyze the copolymerization of CO_2 and epoxides to yield the corresponding polycarbonates with high selectivity at very high

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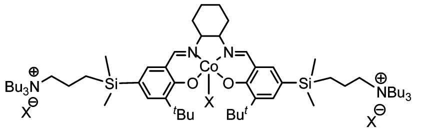
CO_2 pressure (up to 5.5 MPa), these cobalt complexes were proved to be inactive under low CO_2 pressures or at elevated temperature (~50 °C) and unexpectedly reduced to Co(II) derivatives as red solid precipitates, which were ineffective in producing copolymer. The addition of a nucleophilic cocatalyst such as quaternary ammonium halides or sterically hindered strong organic bases could significantly improve the activity even at low CO_2 pressures.[8−10] The nucleophilic cocatalysts were demonstrated to function as an initiator, as well as tentatively thought to stabilize the active SalenCo(III) against decomposition to SalenCo(II).[8,9] In our opinion, the latter role may be more important in maintaining high activity of these Co(III) complexes. Except for this experimental observation, we did not have any direct evidence concerning the role of these nucleophilic cocatalysts in stabilizing active Co(III) species during the copolymerization of CO_2 and epoxides.

Since the coupling reaction of CO_2 with epoxides is exothermic, the development of a thermally robust catalyst is industrially desirable. Five-membered cyclic carbonates are more thermodynamically stable than the corresponding polycarbonates. In addition, the difference in the energies of activation for cyclic carbonate versus copolymer formation in the terminal epoxides such as PO is very small.[14] As a result, the concomitant production of cyclic carbonate easily occurs in the coupling reaction carried out at elevated temperatures. Recently, based on the mechanistic understanding of binary catalyst systems of SalenCoX in conjunction with a quaternary ammonium salt for CO_2/epoxides copolymerization, Lee et al. reported an elegant design of catalyst system **1**. This system contains a Lewis acidic metal center and quaternary ammonium salt units in a molecule that has the highest activity for polycarbonoate synthesis even at high temperatures and high [epoxide]/[catalyst] ratios.[15] The high catalytic activity and polymer selectivity at high temperatures was thought to result from the chain-growing carbonate unit attracted to the metal center through Coulombic interaction between the quaternary ammonium cation anchored on the ligand framework and the chain-growing anion. Further substitution of a small methyl group for the bulky *tert*-butyl group on the 3-position of the aromatic rings significantly enhanced activity, and thereby resulting in the discovery of the fastest catalyst to date.[15b] Prior to this study, Nozaki and co-workers utilized a Salcy-type cobaltate complex **2** with a piperidinium end-capping arm as catalyst for selectively synthesizing aliphatic polycarbonates from CO_2 and terminal epoxides.[16] The high polymer selectivity was achieved based on the proposal that the piperidinium arm controls the formation of cyclic carbonates by protonating the anionic propagating species when they dissociate from the cobalt center. Notably, complete consumption of the epoxide was accomplished with high copolymer selectivity, which allowed for the production of block terpolymers by stepwise addition of two different aliphatic epoxides. Although this cobalt complex was active at 60 °C, there was a concomitant production of cyclic carbonates in the final products (up to 10−40%).[15,16]



X = 2,4-dinitrophenoxy

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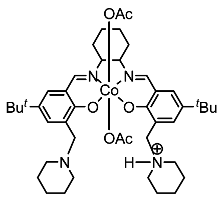

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We have reported that the addition of a nucleophilic cocatalyst could significantly improve the activity of Co(III)−Salen complexes even at low CO_2 pressures and have confirmed its initiator role during CO_2/epoxides copolymerization.[8] Although these studies resulted in the discovery of some highly active catalyst systems,[15] no attempt was made to investigate the mechanistic properties of these nucleophilic cocatalysts for stabilizing active Co(III) species during the copolymerization. Herein, we report a highly active and thermally stable cobalt-based catalyst with 1,5,7-triabicyclo[4,4,0] dec-5-ene (designated as TBD, a sterically hindered organic base) anchored on the ligand framework. This report will provide details of mechanistic studies on the role of the anchored TBD in maintaining high activity and thermal stability of the catalyst during the copolymerization of CO_2 and epoxides. These mechanistic studies are beneficial to elucidating the propagating polymer-chain anion with regard to nucleophilic cocatalysts in previously much-studied binary catalyst systems for stabilizing active Co(III)

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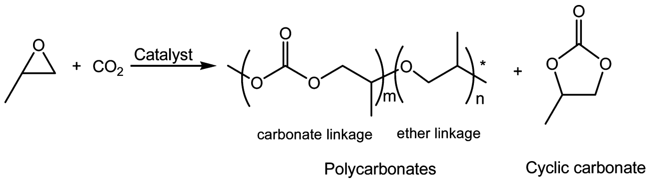
Table 1. CO_2/Propylene Oxide Copolymerization[a]



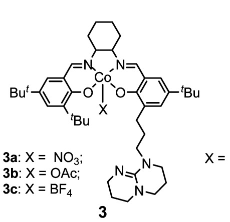
entry	catalyst	PO/catalyst molar ratio	temp (°C)	pressure (MPa)	time (h)	TOF[b] (h^{-1})	selectivity[c] (% polymer)	M_n[d](kg/mol)	PDI[d] (M_w/M_n)
1	**3a**	5000	25	1.5	5.0	432	>99	112.4	1.09
2	**3a**	10000	25	1.5	6.0	410	>99	100.8	1.05
3	**3a**	20000	25	1.5	6.0	425	>99	114.6	1.06
4	**3a**	5000	25	0.6	5.0	428	>99	121.6	1.08
5	**3a**	5000	25	0.1	5.0	265	>99	73.1	1.10
6	**3b**	10000	25	1.5	4.0	612	>99	134.6	1.09
7	**3c**	5000	25	1.5	6.0	13	70	-	-
8	**3b**	10000	50	1.5	2.0	1923	>99	148.7	1.12
9	**3b**	10000	80	2.0	0.5	6290	98	101.2	1.18
10	**3b**	10000	90	2.0	0.25	8235	98	85.4	1.15
11	**3b**	25000	90	2.0	1.0	7139	97	112.3	1.18
12	**3b**	10000	100	2.5	0.25	10882	97	60.2	1.23
13[e]	**1**	25000	90	2.0	1.0	3500	90	80.0	1.32
14[e]	**2**	25000	80	2.0	3.0	370	60	-	-
15	**4**	10000	80	2.0	0.5	3863	95	62.3	1.29
16	**5**	10000	25	1.5	6.0	25	64	-	-
17	**6**	10000	25	1.5	6.0	7	0	-	-
18	7	10000	25	1.5	6.0	41	85	7.8	1.20

[a] The reaction was performed in neat propylene oxide (PO) (14 mL, 200 mmol) in 75 mL autoclave. Carbonate linkages of the resulted polycarbonates are >99% based on ^1H NMR spectroscopy. [b] Turnover frequency of PO to products (polycarbonate and cyclic carbonate). [c] Determined using ^1H NMR spectroscopy. [d] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [e] Data from ref 15a.

species, and provide insight as to how these cobalt-based catalyst systems operate during the copolymerization.

Results and Discussion

The unsymmetrical Schiff-base ligands in the complexes **3**−**6** were synthesized by the reaction of the corresponding functional salicyaldehydes with the condensation product of 1,2-diaminocyclohexane mono(hydrogen chloride) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (detailed synthesis procedure, see Supporting Information). Since these cobalt complexes **3**−**8** are easily dissolved in neat epoxides surveyed, the catalyzed coupling of CO_2 and epoxides does not require any organic cosolvent. Only in some cases for complete conversion of epoxides, the addition of an organic solvent such as 1,2-dimethoxyethane is necessary for effective diffusion of the reactants.



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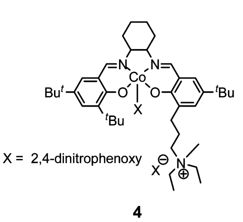

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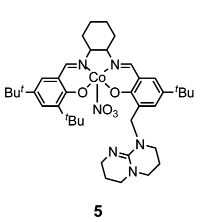

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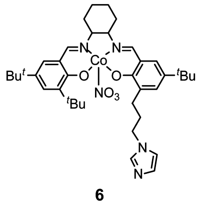

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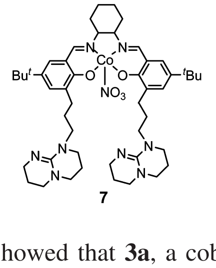

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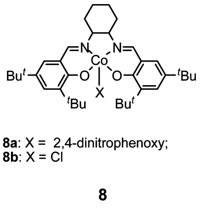

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Our initial studies showed that **3a**, a cobalt-based complex with an anchored sterically hindered TBD on its ligand framework, could effectively catalyze CO_2/PO copolymerization to selectively afford the corresponding copolymer with more than 99% carbonate linkages at a high [epoxide]/[catalyst] ratio of 5000 under a CO_2 pressure of 1.5 MPa and at ambient temperature (Table 1, entry 1). The catalyst activity is about 6 times that of our previously reported binary catalyst system of the complex **8a** in conjunction with 7-methyl-1,5,7-triazabicyclo[4.4.0] dec-5-ene (MTBD) under the same conditions in which the initiator role of MTBD was confirmed by electrospray ionization mass spectrometry (ESI-MS).[8b] With further increase in the molar ratio of epoxide to catalyst, no obvious change in copolymerizaiton rate and polymer selectivity was observed in this reaction (entries 2 and 3). The isolated polymers have narrow molecular-weight distributions less than 1.1, but the M_n values are not close to the expected values, which indicate the existence of chain transfer during the reaction.[17] Indeed, although every effort has been made to keep the copolymerization reaction anhydrous, we were concerned that trace quantities of water might be present which could have a deleterious effect on the reaction rate.[2g,18] Furthermore, in the presence of an organic solvent such as 1,2-dimethoxyethane, quantitative conversion of the epoxide was achieved with high polymer selectivity by a prolonged reaction time. Although the M_n values are not close to the expected values due to chain transfer caused by trace quantities of water in the copolymerization system, the chain transfer does not result in chain termination and the dissociated chain can repropagate when

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(17) Although PO was refluxed over a mixture of KOH/CaH_2 for more than 10 h, the water content in the epoxide was in the range of 20−25 ppm, which was determined by means of Karl−Fischer coulometry. In most experiments, the resulted copolymers exhibited bimodal distribution, but with a prolonged reaction time, the proportion of the higher-molecular-weight copolymers decreased and the PDIs became narrower.

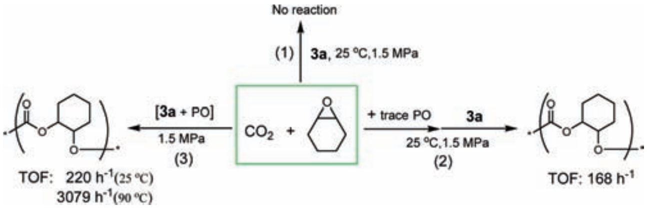
(18) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026–14038.

activated on a catalyst center. The polymer molecular weight is linearly proportional to the conversion, and its distribution is less than 1.1. This is consistent with an immortal polymerization (a living polymerization that involves rapid and reversible chain transfer), which allows for the production of block terpolymers by stepwise addition of two different epoxides.[2c,16] Noteworthy successes were realized for the synthesis of various block terpolymers without sacrificing polymer selectivity, which will be published elsewhere.

We were gratified to discover that the catalyst system can operate at high efficiency with CO_2 at atmospheric pressure, with a turnover frequency (TOF) up to 265 h^{-1} at 25 °C. Significantly, the variation of CO_2 pressure does not lead to an observable decrease in selectivity for PPC formation (entries 4 and 5). This is distinct from the previously reported catalyst systems using zinc or chromium complexes,[7,19] in which an increase in the pressure of CO_2 is beneficial for suppressing cyclic carbonate formation and effectively increases the selectivity for polymer while moderately decreasing the catalyst activity for PPC formation. The nucleophilicity of the axial anion of cobalt(III) complexes has a significant influence on CO_2/PO copolymerization (entries 2, 6, and 7). A change in the axial anion from NO_3^- to more nucleophilic CH_3COO^- increases the TOF from 410 to 612 h^{-1} at a [PO]/[catalyst] ratio of 10000 at ambient temperature, while substituted non-nucleophilic BF_4^- for NO_3^- caused nearly complete loss in catalyst activity (entry 7). The reaction temperature has a strong influence on the rate (entries 6, 8−12). For example, with **3b** as catalyst at a [PO]/[catalyst] ratio of 10000, an increase in the temperature from 25 to 90 °C resulted in a dramatic increase of TOF from 612 to 8235 h^{-1}. Notably, the polycarbonate selectivity of up to 97% and an activity more than 10000 h^{-1} were achieved when the copolymerization reaction was performed at a high temperature of 100 °C. It is worth noting here that a decrease in polycarbonate molecular weight and a slight increase in polymer molecular-weight distribution were observed at enhanced reaction temperatures. A similar decrease in polymer molecular weight was also observed in the binary catalyst systems of SalenCoX in conjunction with quaternary ammonium halides or sterically hindered strong organic bases for this reaction.[8b] We suspect that, aside from trace water, perhaps the elevated temperature causes the dissociation of the initiating anion from the propagating polymer chain and thereby results in the molecular weight discrepancy.[20]

Stimulated by our success with these cobalt-based catalyst systems for the alternating copolymerization of CO_2 and PO, we likewise applied these systems to the copolymerization of alicyclic cyclohexene oxide (CHO) and CO_2. Unfortunately, neither copolymer nor cyclic carbonate was observed in the system with the use of **3a** as catalyst at various temperatures. Interestingly, the addition of trace amounts of PO resulted in rapid conversion of CHO to the corresponding polycarbonate even at ambient temperature and low CO_2 pressure (Scheme 1). The completely alternating nature (>99% carbonate linkages) of the resulting polymer was reflected in the presence of the methine proton peak in the cyclohexene carbonate unit at a chemical shift of 4.65 ppm and the absence of that peak in the repeating oxy(1,2-cyclohexene) unit (ether linkage) at 3.45 ppm in the ^1H NMR spectra. Both samples from the initial period and after the reaction were analyzed by ESI-MS. No propagating polymer species consistent with TBD anchored on the ligand framework of **3a** was found and only one species of *m*/*z* 784.5 was clearly observed in the positive-mode ESI tandem mass spectra of all tested samples. When the complex **3a** was first treated with PO followed by the complete removal of the residual PO from the **3a**/PO mixture system via vacuum, a species of *m*/*z* 784.5 was observed in the mass spectra. The resulting solid was found to be more efficient for catalyzing CO_2/CHO copolymerization to selectively produce the corresponding polycarbonates with >99% carbonate linkages and high catalytic activities up to 220 h^{-1} (TOF) at ambient temperature and 3079 h^{-1} at 90 °C. This was achieved without sacrificing polymer selectivity (Scheme 1), and proved to be the highest record in this polymerization.[21]

Scheme 1. The Copolymerization of CO_2 and Cyclohexene Oxide (CHO) Catalyzed by the Complex **3a** at Various Conditions[a]



[a] All polymerizations were performed in neat epoxide with [CHO]/[Co] = 5000. Turnover frequency: moles of CHO consumed per mole of metal per hour. Carbonate linkages of the resulted polycarbonates are >99% based on ^1H NMR spectroscopy.

Advances in polymer chemistry rely not only on revolutionary catalyst discoveries, but also a detailed analysis of the catalytic mechanism and its refinement.[22] This research can provide considerable insight concerning catalyst design and modification and therefore help in the development of commercial applications. The production of polycarbonates from CO_2/epoxides copolymerization is based upon Inoue's discovery of the heterogeneously catalyzed copolymerization of CO_2 and PO to give PPC with a very low reaction rate (TOF: 0.12 h^{-1}).[23] Following this discovery, numerous heterogeneous and homogeneous catalyst systems have been developed for this trans-

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(19) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284–14285.

(20) In previous paper, we have confirmed the initiator role of MTBD in the binary **8a**/MTBD catalyst system for CO_2/PO copolymerization by ESI-MS, and further demonstrated the living polymerization characteristics in the measurable range of the instrument (see ref 8b). In the ESI-Q-TOF mass spectra in positive ion mode, we observe the species of $[MTBD + H^+]$, $[MTBD + PO + H^+]$ and $[^-OCH(CH_3)CH_2\text{-}(CO_2\text{-}alt\text{-}PO)_n\text{-}MTBD^+ + H^+]$, but with time, the former two species gradually disappear and the latter species re-moves to high *m*/*z* region. After no species with regard to MTBD was observed, the reaction system was heated to 60 °C, and the species of $[MTBD + H^+]$, $[MTBD + PO + H^+]$, and $[^-OCH(CH_3)CH_2\text{-}(CO_2\text{-}alt\text{-}PO)_n\text{-}MTBD^+ + H^+]$ appeared in the ESI-MS spectra again (see Supporting Information, Figure S1). This result indicates that the elevated temperature causes the dissociation of the MTBD initiator from the propagating polymer-chain.

(21) Indeed, only limited catalysts exhibit certain activities for CHO/CO_2 copolymerization at room temperature and relatively low CO_2 pressure, probably due to the more sterically hindered, less reactive CHO monomer. For example, Williams and co-workers recently reported a novel macrocyclic dizinc catalyst for CHO/CO_2 copolymerization, and an activity of 24 h^{-1} (TOF) was achieved at 1 atm pressure and 90 °C (see ref 5j). Also, the catalyst system (**3**) in Scheme 1 was performed at 0.1 MPa, and the TOF up to 153 h^{-1} was obtained at ambient temperature.

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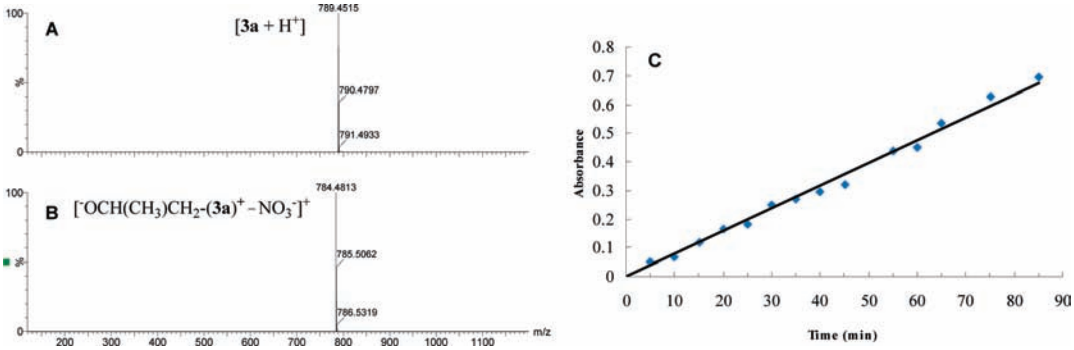

Figure 1. (A) ESI-Q-TOF mass spectrum of **3a**; (B) representative ESI-Q-TOF mass spectrum of the reaction mixture of PO and CO_2 catalyzed by **3a** (**3a**/PO = 1/10000, molar ratio) at 25 °C and at 1.5 MPa; and (C) a time profile of the absorption at 1750 cm^{-1} (corresponding to polycarbonate) of the reaction mixture diluted by CH_2Cl_2.

formation.[1] Prominent among these systems are discrete zinc phenoxides, β-diiminate zinc alkoxides, and binary or bifunctional catalyst systems based on metal−Salen complexes being the most efficient for the CO_2/epoxides coupling reactions.[3,4,8,9,15,16] It is worth mentioning that some elegant mechanism studies contributed significantly to the discovery of these highly active catalyst systems.[19,24−28] As to the binary or bifunctional catalyst systems based on cobalt−Salen complexes, the observation that the addition of a nucleophilic cocatalyst significantly improves the activity of cobalt−Salen complexes even at low CO_2 pressure has remained poorly understood. Although the nucleophilic cocatalysts were tentatively thought to stabilize the active SalenCo(III) species against decomposition to inactive SalenCo(II), no direct evidence was obtained for supporting this hypothesis. The current study seeks to understand how these cobalt-based catalyst systems operate, by investigating what role the anchored TBD of the complex **3a** or **3b** plays in maintaining its thermal stability and high activity in CO_2/epoxides copolymerization.

Electrospray ionization (ESI) is a soft ionization method that can keep any weakly bound ligand intact in a complex ion. This property has enabled ESI to become increasingly popular as an analytical tool in inorganic/organometallic chemistry.[29] ESI, in combination with tandem mass spectrometry (MS/MS), has been employed to study mechanistic aspects of some homogeneously catalyzed reactions including Ziegler−Natta polymerization of olefins.[30,31] In the recent report of Chen et al., the binding of aliphatic epoxides to SalenM(III) cations (where M = Cr, Co, Ga, and Al) was studied in the gas phase by electrospray tandem mass spectroscopy. The results were discussed in terms of the reactivity of these complexes in the ring-opening polymerizations of epoxides and copolymerizations with CO_2, respectively.[32] In the present paper, we also performed ESI-MS in positive-mode for continuous determination of the transient cationic species at various time points. In sharp contrast to the binary **8a**/MTBD catalyst system utilizing the complex **3a** as catalyst with a [PO]/[catalyst] ratio of 10000, we did not observe the propagating polymer species with TBD anchored on the ligand framework of **3a** but found only one species of *m*/*z* 784.5 (Figure 1B). It should be noted that continuous Fourier transform infrared spectroscopy (FTIR) determination of intensity at 1750 cm^{-1} at various time points demonstrated that the copolymerization reaction promptly occurred after CO_2 was charged into the system (Figure 1C). To our surprise, even after complete conversion of PO in the system with 1,2-dimethoxyethane as organic solvent, the species of *m*/*z* 784.5 could be clearly observed in the positive-mode ESI tandem mass spectra. When the molar ratio of PO to **3a** was reduced to 2000, apart from the species of *m*/*z* 784.5, weak signals of the propagating polymer species $[^{-}OCH(CH_3)CH_2-(CO_2\text{-}alt\text{-}PO)_n\text{-}(\mathbf{3a})^+ - NO_3^-]^+$ with regard to TBD anchored on the ligand framework of **3a** were observed in the positive-mode ESI-MS spectra of the reaction mixture (see Supporting Information Figure S3).

To further the investigation of the *m*/*z* 784.5 species, we studied the reaction of **3a** with PO in the absence of CO_2 by ESI-MS spectroscopy. We detected two species of *m*/*z* 784.5 and 726.5. The latter species rapidly disappeared with time. This suggests that the formation of the species of *m*/*z* 784.5 is a fast reaction (Figure 2A). The species of *m*/*z* 784.5 was characterized by collision-induced dissociation (CID). This analysis did not result in any scission even via CID experiments up to 15 V, indicating that *m*/*z* 784.5 is highly stable (Figure 2B). These results demonstrate that the species of *m*/*z* 784.5 in Figure 1B can be ascribed to $[^{-}OCH(CH_3)CH_2-(\mathbf{3a})^+ - NO_3^-]^+$.

Since the complex **3a** did not initiate the homopolymerization of PO, we can investigate the insertion of CO_2 into the Co−O bond using the *in situ* FTIR method by monitoring the $\nu(CO_2)$ region of the infrared spectra. After only the species of *m*/*z* 784.5 was observed in the mass spectra, complete removal of PO from the **3a**/PO mixture system was performed via a vacuum and the resulting solid was dissolved in anhydrous CH_2Cl_2. When the solution was bubbled with CO_2, two equivalent

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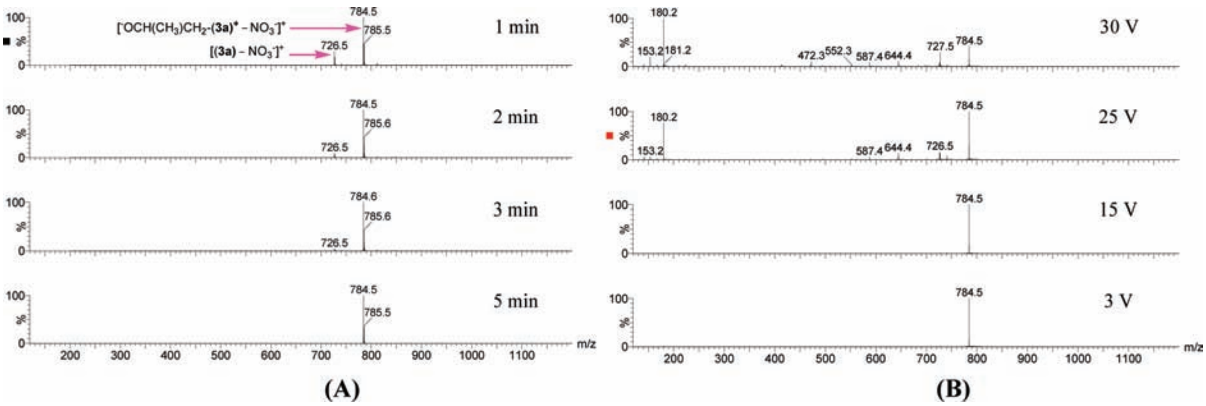

Figure 2. (A) ESI-Q-TOF mass spectra of the mixture solution of PO/**3a** (10000, molar ratio) at 20 °C with various time points after **3a** was dissolved into PO; and (B) collision-induced dissociation (CID) of the species of *m*/*z* 784.5 resulted from the system of PO/**3a** (10000, molar ratio) at 20 °C with various voltages (diluted with CH_2Cl_2).

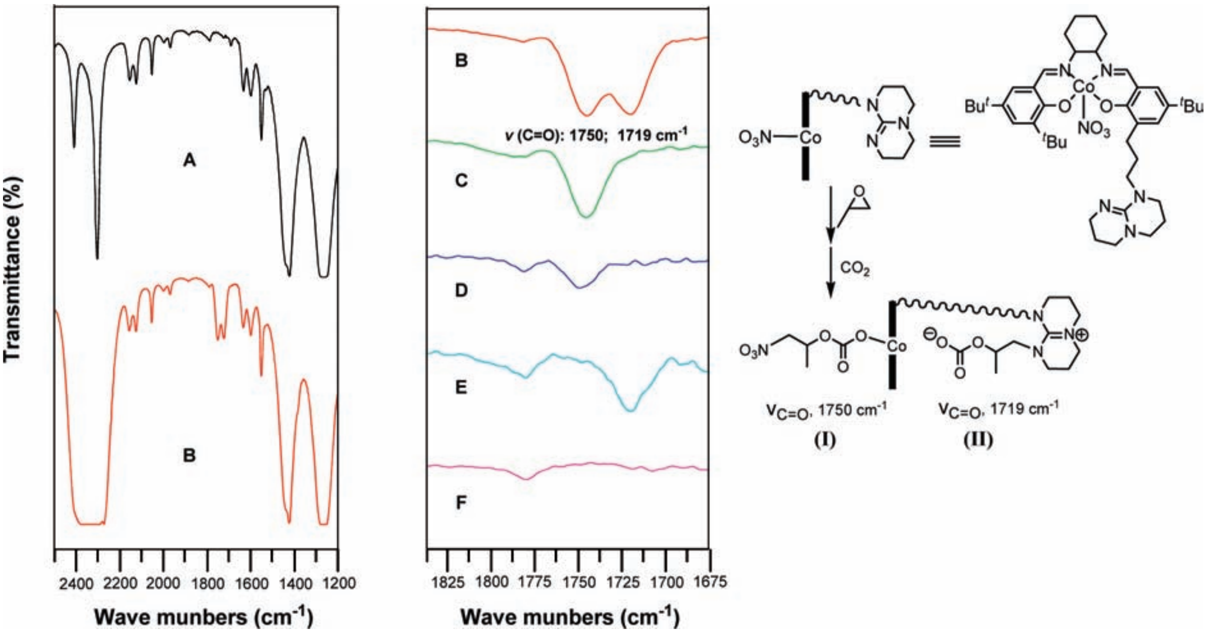

Figure 3. FTIR spectra of (A) the CH_2Cl_2 solution of the solid product obtained by the complete removal of the residual PO from the **3a**/PO mixture (PO/**3a** = 10000, molar ratio) solution; (B) after bubbling CO_2 through the (A) solution; (C) after bubbling N_2 through the (B) solution; (D) after the (C) solution was heated at 60 °C for 30 min; (E) after bubbling CO_2 through the CH_2Cl_2 solution of the solid product obtained by the complete removal of PO from the **3c**/PO mixture (PO/**3c** = 10000) solution; (F) after bubbling N_2 through the (E) solution.

absorption peaks at 1750 and 1719 cm^{-1} were found in the FTIR spectrum (Figure 3B).[33] Interestingly, the bubbling of N_2 for removing the free CO_2 from the solution resulted in the complete disappearance of the absorption at 1719 cm^{-1} but no obvious change in the absorption at 1750 cm^{-1} (Figure 3C). If the FTIR sample was heated at 60 °C, a significant decrease in the intensity at 1750 cm^{-1} was also observed (Figure 3D). To confirm the identifications of the two absorption peaks, we further performed a similar experiment with the substitution of **3c** for **3a**. Only one absorption peak at 1719 cm^{-1}, which is also easily removed by bubbling N_2 into the system, was observed in the spectrum after the addition of CO_2 into the CH_2Cl_2 solution of the cobalt complex formed from the reaction of **3c** and PO (Figure 3E,F). It is generally known that non-nucleophilic BF_4^- anion cannot initiate the copolymerization of CO_2 with PO. Therefore, we can conclude that the two equivalent absorption peaks at 1750 and 1719 cm^{-1} in the former system originate from the vibrations of C═O in carboxylate (I) and (II) (Figure 3), respectively. These results lead us to conclude that the species of *m*/*z* 784.5 in Figure 2B assigned to $[^-OCH(CH_3)CH_2-(\mathbf{3a})^+ - NO_3^-]^+$ predominantly results from the dissociation of the real species $[^-OOCOCH(CH_3)CH_2-(\mathbf{3a})^+ - NO_3^-]^+$,[34] due to its low collision dissociation energy and the effect of ESI gas of N_2. Therefore, we can reasonably assume

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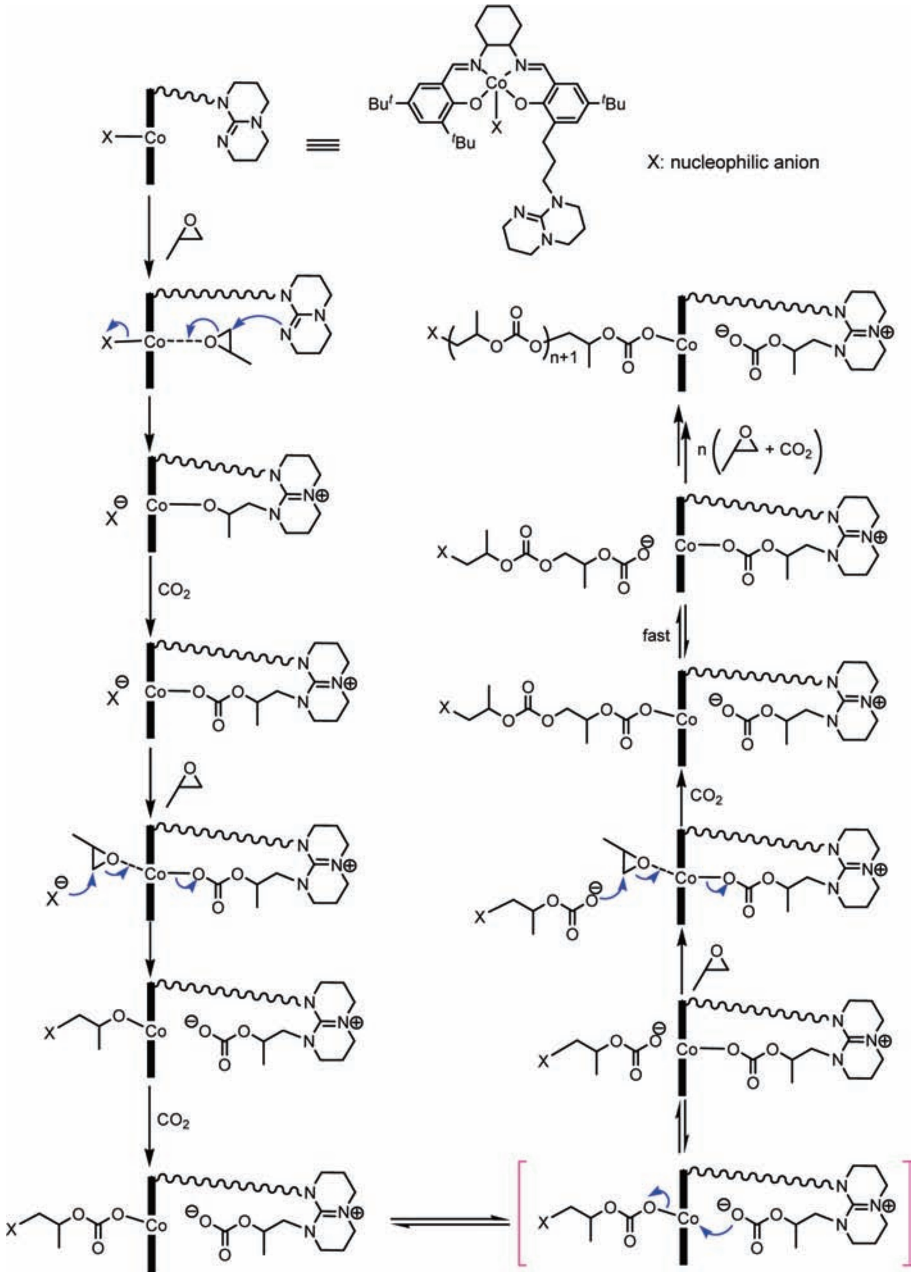
[33] Darensbourg et al. have investigated the interaction of CO_2 with 4-(dimethylamino)pyridine (DMAP) in the presence of chromium Salen complex by in situ infrared spectroscopy, and observed several new bands at 1650, 2097, and 2018 cm^{-1}, in which the two latter signals were assigned to CO_2 insertion into a metal−amide bond. Also the authors further concluded from some control experiments that bicarbonate generated by adventitious water was not likely the cocatalyst in the catalyst systems which consisted of SalenCr(III) and DMAP for CO_2/epoxides copolymerization (See ref 18).

[34] Recently, Luinstra et al. reported the mechanism understanding on the formation of aliphatic polycarbonates from aliphatic epoxides and CO_2 copolymerization with chromium(III) and aluminum(III) metal−Salen complexes by a DFT theoretical calculation method, in which they also proposed the propagating carboxylate easily dissociating from the metal center during the copolymerization (see ref 27).

Scheme 2. Mechanistic Understanding on the Role of the Anchored TBD on the Ligand Framework of the Complex **3** (**3a** or **3b**) during CO_2/PO Copolymerization



that the species $[^{-}OOCOCH(CH_3)CH_2-(\mathbf{3a})^{+} - NO_3^{-}]^{+}$ with respect to the anchored TBD on the ligand framework helps to stabilize the active Co(III) species by reversible intramolecular Co−O bond formation and dissociation (Scheme 2).

It is worth noting that the length of the spacer linked ligand framework and TBD plays an important role in maintaining high activity. A flexible and sufficiently long spacer is usually a prerequisite for obtaining excellent catalytic activity at high [epoxide]/[catalyst] ratio. The activity of the complex **5** with the methylene spacer is less than 1/10 that of **3a** under the same conditions (Table 1, entry 16), and the corresponding Co(II) complex was unexpectedly observed after the reaction. When the molar ratio of [PO]/**5** is 10000, we did not detect the species of *m*/*z* 756.5 assigned to $[^{-}OCH(CH_3)CH_2-(\mathbf{5})^{+} - NO_3^{-}]^{+}$, but clearly observed the species of 699.5, which is ascribed to the corresponding Co(II) complex (Figure 4B). This result indicates that the anchored TBD on the ligand framework of the complex **5** does not stabilize the active Co(III) species.

Surprisingly, substituted imidazole (a coordination base, **6**) for sterically hindered TBD anchored on the ligand framework of the complex **3a** resulted in nearly complete loss in activity at ambient temperature (entry 17). As anticipated, in the presence of 2 equiv of *N*-methylimidazole, the complex **3a** also did not show any activity for this reaction under the same conditions. This could be due to the coordination of *N*-methylimidazole to the central metal ion and thereby retarding the activation of the epoxide. These results indicate that the steric repulsion originating from TBD effectively inhibits its coordination to Lewis acidic metal ion and benefits the formation of the carboxylate intermediate with regard to the anchored TBD, which efficiently stabilizes the active Co(III) species during the copolymerization. For a comparison purpose, the cobalt complex **7** with two

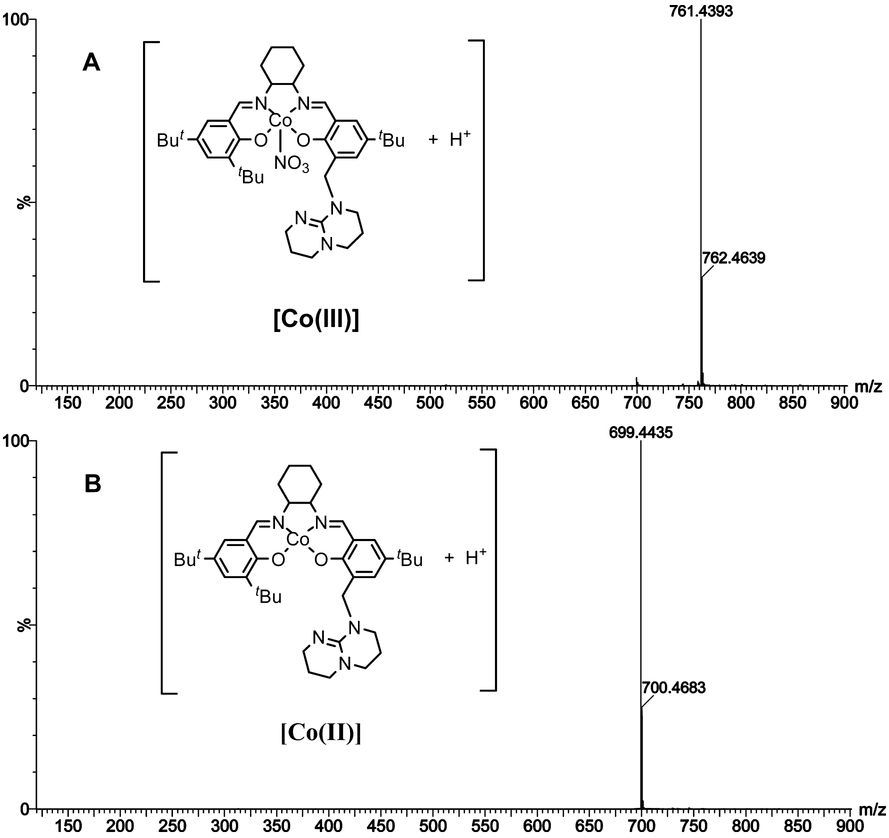


Figure 4. ESI-Q-TOF mass spectra of (A) the complex **5** in CH_2Cl_2, and (B) the reaction mixture of PO and CO_2 catalyzed by the complex **5** (**5**/PO = 1/10 000, molar ratio) at 25 °C and 1.5 MPa.

anchored TBD groups was synthesized and tested for catalyzing the CO_2/PO copolymerization (entry 18). Unfortunately, the complex **7** did not exhibit high activity for this reaction, perhaps due to the intramolecular actions of the two anchored TBD carbonate chain with the central metal ion. This would retard coordination activation of the epoxide and thereby significantly affecting polymer-chain growth.

On the basis of the facts described above, a reaction mechanism is proposed and shown in Scheme 2, in which the anchored TBD on the ligand framework of **3a** or **3b** helps to stabilize the active Co(III) species against decomposition to inactive Co(II) by reversible intramolecular Co−O bond formation and dissociation. In the initial stage, the epoxide first coordinates to the active metal center trans to the axial anion and is further ring-opened by nucleophilic attack of the anchored TBD. In the meantime, the coordination of the epoxide and its further ring-opening also labilize the Co−X bond and thereby promote the leaving of the axial X anion. Then, CO_2 rapidly inserts into the Co−O bond and another epoxide coordinates the central metal ion trans to the formed carboxylate species with regard to the anchored TBD. The ring-opening of the coordinated epoxide attacked by the nucleohilic X anion is beneficial to the dissociation of the carboxylate species with regard to the anchored TBD. The insertion of CO_2 to Co−O bond produces the linear carbonate associated with the axial X anion, which easily dissociates from the central metal due to the reversible coordination of the dissociated carboxylate species with respect to the anchored TBD. The observation that the polycarbonate products contained more than 99% carbonate linkages suggests that the insertion of CO_2 to Co−O bond is a fast reaction and that the dissociation of propagating carboxylate species from the central metal ion as well as the coordination activation of an epoxide and its further ring-opening is a key step during the copolymerization reaction. The ring-opening of the coordinated epoxide attacked by the carbonate anion of the dissociated polymer-growth chain derived from the axial anion results in the dissociation of the carboxylate intermediate with regard to the TBD anchored on the catalyst ligand framework. The dissociated carbonate anion derived from the anchored TBD recoordinates the Lewis acidic metal center, and thereby facilitates the dissociation of its trans propagating carboxylate species. More importantly, the recoordination of the carboxylate intermediate associated with the anchored TBD helps to stabilize the active Co(III) species against decomposition to inactive Co(II). Although the imidazole anchored on the ligand framework in the complex **6** can also stabilize the Co(III) state efficiently, its strong coordination to the central metal ion significantly decreases the Lewis acidity of the cobalt ion. This has a negative effect on the epoxide activation and the polymer-chain growth trans to the coordinated imidazole. It is should be noted that the complex **3a** did not exhibit any activity in the coupling reaction of alicyclic cyclohexene oxide (CHO) and CO_2 (Scheme 1), in which the species of 727.7 ascribed to the corresponding Co(II) complex was clearly observed in the ESI-MS spectrum of the reaction mixture (Figure 5). When the reaction was performed for only 2 h, the Salen−Co(III) species were completely transformed into the corresponding Co(II) species (Figure 5B). Indeed, the intramolecularly nucleophilic attack of the TBD anchored on the ligand framework of the complex **3a** at the coordinated CHO on the central metal ion rarely occurs due to their steric hindrances, and thus, the anchored TBD has no positive effect on stabilizing the active Co(III) species. On the contrary, in the presence of trace PO or the treatment of complex **3a** with PO, the copolymerization of

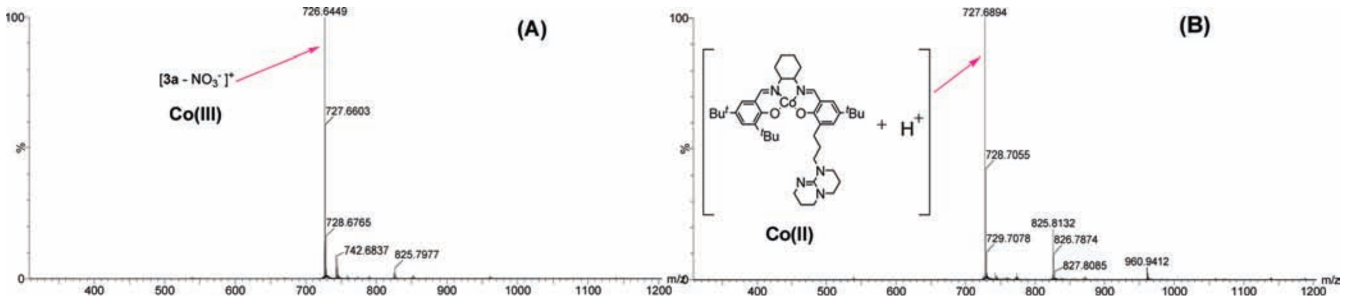


Figure 5. Detailed ESI-Q-TOF mass spectra of the reaction mixture of CHO and CO_2 catalyzed by **3a** (**3a**/CHO = 1/5000, molar ratio) at 25 °C with various time points: (A) 5 min, and (B) 2 h (diluted with CH_2Cl_2).

CO_2 and CHO run smoothly. This suggests that the formed carboxylate intermediate with respect to the anchored TBD helps to stabilize the active Co(III) species against decomposition to inactive Co(II) by reversible intramolecular Co−O bond formation and dissociation during the reaction.

This mechanism also can explain how the addition of a nucleophilic cocatalyst such as quaternary ammonium halides or sterically hindered strong organic bases could significantly improve the activity of Co(III)−Salen complexes. A new mechanistic understanding concerning binary or bifunctional catalyst systems based on Co(III)−Salen complexes is shown in Scheme 3. Alternating chain-growth and dissociation of propagating carboxylate species derived from the nucleophilic axial anion and the cocatalyst take turns at both sides of the Co(III)−Salen center. This significantly increases the reaction rate and also helps to stabilize the active Co(III) species against decomposition to inactive Co(II) even at low CO_2 pressures and/or relatively high temperatures. In support of this hypothesis, some control experiments were performed and the results are listed in Table 2. As previously reported,[8] in the absence of a nucleophilic cocatalyst, the complex **8a** could not effectively catalyze CO_2/PO copolymerization at 1.5 MPa pressure and predominately decomposed to inactive Co(II) species. The addition of 1 equiv of ^{n}Bu$_4$NX (X = 2,4-dinitrophenoxy anion) significantly improved the catalytic activity of **8a** at ambient temperature (Table 2, entries 2 and 3). A decrease in the molar ratio of PO to **8a** from 10 000 to 2000 results in a TOF of 90 h^{-1} increasing to 204 h^{-1}. High cocatalyst loading makes a contribution to the increase in catalytic activity of **8a**, but it has a negative effect on the selectivity for polymer formation (entries 4 and 6). It can be tentatively assumed that the nucleophilic attack of the cocatalyst or the dissociated propagating carboxylate species at the activating PO by its coordination to the central metal ion of **8a** is similar to a bimolecular process. Therefore, the rate is proportional to the concentration of the propagating species consistent with the cocatalyst and the nucleophilic axial anion, as well as that of the activating PO with regard to the complex **8a**. On the other hand, high cocatalyst loading is beneficial to stabilizing the active Co(III) species at high [epoxide]/[catalyst] ratio and, thus, results in a high rate in the CO_2/epoxides copolymerization. Recently, combined NMR and quantum chemical studies by Kemper et al. demonstrated that an equilibrium between the paramagnetic and diamagnetic complexes could be observed for **8b** in THF (the coordination properties of THF and epoxides are comparable) over a range of temperature, yielding paramagnetic NMR spectra at increased temperature.[35] With regard to the bifunctional catalyst systems (the complexes **1** and **4**) containing a Lewis acidic metal center and quaternary ammonium salt units

Scheme 3. Mechanistic Understanding of Binary Catalyst Systems Based on SalenCo(III) for CO_2/PO Copolymerization

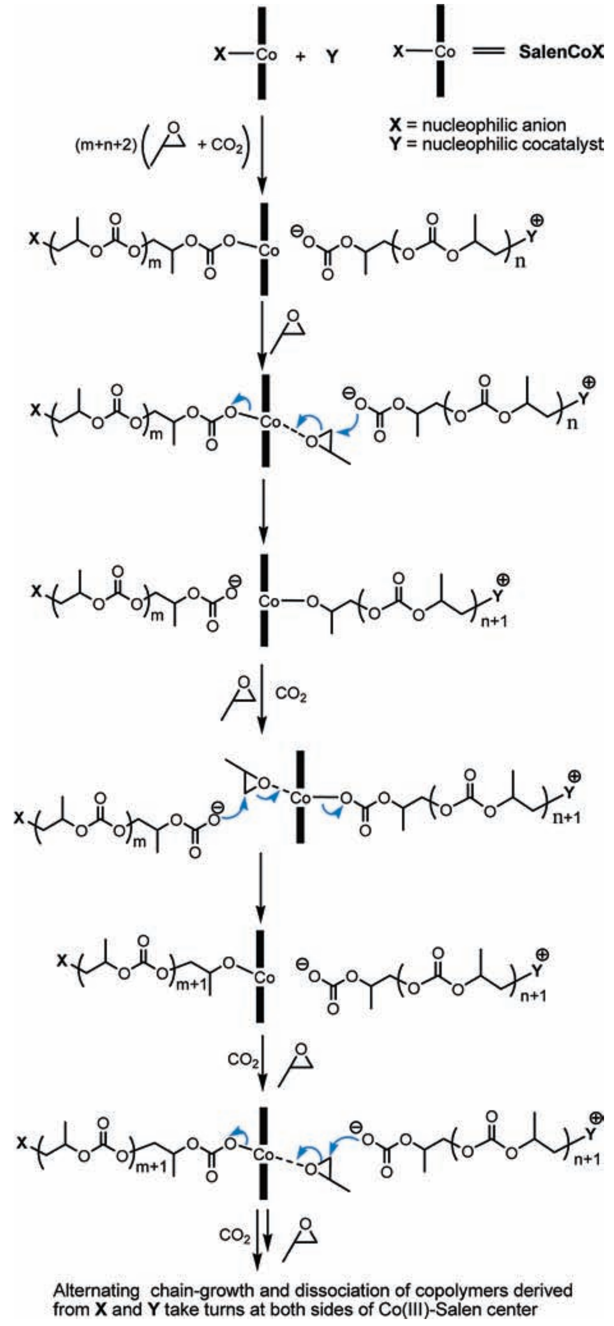


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Table 2. CO_2/PO Copolymerization Catalyzed by the Complex **8a**[a]

entry	cocatalyst (equiv)	PO/**8a** molar ratio	temp (°C)	time (h)	TOF[b] (h^{-1})	selectivity[c] (% polymer)	M_n[d](kg/mol)	PDI[d] (M_w/M_n)
1[e]	-	10000	25	10.0	<5	-	-	-
2	$^{n}Bu_4NX$ (1)	10000	25	10.0	90	99	28.9	1.04
3	$^{n}Bu_4NX$ (1)	2000	25	4.0	204	>99	30.4	1.10
4	$^{n}Bu_4NX$ (10)	10000	25	6.0	560	94	28.8	1.13
5	$^{n}Bu_4NX$ (1)	10000	60	7.0	656	90	46.3	1.15
6	$^{n}Bu_4NX$ (10)	10000	60	3.5	1540	63	-	-

[a] The reaction was performed in neat propylene oxide (PO) (14 mL, 200 mmol) in 75 mL autoclave at 1.5 MPa CO_2 pressure. [b] Turnover frequency of PO to products (polycarbonate and cyclic carbonate). [c] Determined by using ^{1}H NMR spectroscopy. [d] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [e] Co(II) derivative was predominantly produced.

in a molecule, the interaction between the quaternary ammonium cation anchored on the ligand framework and the propagating carbonate anion leads to the dissociated carboxylate species always hanging around the metal center, and thereby helps to stabilize the active Co(III) species even at enhanced temperature and/or high [epoxide]/[catalyst] ratio.[15] Therefore, one major difference between the much-studied binary and bifunctional catalyst system is the counter cations of the dissociated anions. In the binary system, the countercation is not linked intramolecularly with the cobalt complex. Thus, the ion pair of the countercation and the dissociated anion can be far away from the cobalt center, particularly under highly diluted solution and/or at high reaction temperatures. In contrast, in the bifunctional catalyst system, the cobalt complex with quaternary ammonium moiety can keep the dissociated anion around itself, resulting in higher stability and catalytic activity. For the present system involving the complex **3a** or **3b**, in which the iminium moiety can also keep the dissociated anion around itself, only one initiating anion exists in the cobalt complex that is beneficial to maintaining polymer selectivity and narrow molecular-weight distribution even at high temperatures (Table 1, entries 9−15). Notably, it is more efficient that the TBD-linked carboxylate group stabilizes the active Co(III) species by reversibly intramolecular coordination to the cobalt center.

Conclusion

In conclusion, we have developed a novel single-site, cobalt-based catalyst with a sterically hindered TBD anchored on the ligand framework for CO_2/epoxides copolymerization. This catalyst exhibits highly active and selective polymer formation even at high temperatures (up to 100 °C), high [epoxide]/[catalyst] ratios, and/or low CO_2 pressures. The anchored TBD on the ligand framework plays an important role in maintaining thermal stability and high activity of the catalyst. Continuous monitoring of the reaction mixture at various time points was achieved by ESI-MS. This analysis in combination with *in situ* FTIR studies and some control experiments provided us with insight into the mechanistic properties of the CO_2/epoxide copolymerization reaction. We found that the carboxylate intermediate with regard to the TBD anchored on the catalyst ligand framework helps to stabilize the active Co(III) species against decomposition to inactive Co(II) by reversibly intramolecular Co−O bond formation and dissociation. The cobalt complex with iminium moiety can keep the dissociated anion around itself, resulting in higher stabilizing ability and catalytic activity. The sole initiating anion of the cobalt complex is beneficial to maintaining polymer selectivity and narrow molecular-weight distribution even under highly diluted solution and/or at high reaction temperatures. These studies provide a new mechanistic understanding of our previously studied binary catalyst systems based on Co(III)−Salen complexes in which alternating chain-growth and dissociation of propagating carboxylate species derived from the nucleophilic axial anion and the nucleophilic cocatalyst take turns at both sides of the Co(III)−Salen center. This arrangement significantly increases the reaction rate and also helps to stabilize the active Co(III) species against decomposition to inactive Co(II) even at low CO_2 pressures and/or relatively high temperatures.

Acknowledgment. This work was supported by National Natural Science Foundation of China (NSFC) program (Grant 20634040) and National Basic Research Program of China (973 Program: 2009CB825300). Xiao-Bing Lu gratefully acknowledges the Outstanding Young Scientist Foundation of NSFC (Grant 20625414).

Supporting Information Available: General experimental procedures, full experimental details on the preparation of all ligands and their cobalt complexes, detailed ESI-Q-TOF mass spectra at various time, and characterization of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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