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Lanthanide Complexes Supported by a Trizinc-crown Ether as Catalysts for Alternating Copolymerization of Epoxide and CO_2: Telomerization Controlled by Carboxylate Anions

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Abstract: A new family of heterometallic catalysts based on trimetallated macrocyclic tris(salen) ligands and rare earth metal was prepared and structurally characterized. The $LaZn_3$ system containing anionic ligands such as acetate play a critical role in catalyzing alternating copolymerization of cyclohexene oxide (CHO) and CO_2 with a high carbonate linkage. Among lanthanide metals, the $CeZn_3$ system exhibits high catalytic activity with TOF over 370 h^{-1}. NMR analysis of the complex and end-group analysis of the polymer suggested that the acetate ligands are rapidly exchanged, not only among coordinated acetates, but also between coordinated acetates and added carboxylate anions. Such unique properties provide the first example of telomerization for copolymerization of CHO and CO_2 by adding excess amounts of ammonium carboxylates to control the molecular weight of the polymer.

Since 1969, when Inoue *et al.* discovered a heterogeneous catalyst of $ZnEt_2/H_2O$ for the copolymerization of epoxides with CO_2 to give alternating copolymers,[1] several heterogeneous and homogeneous catalyst systems have been intensively investigated toward developing a promising process to convert CO_2 into biodegradable polymers. In addition to heterogeneous catalysts based on zinc,[2] double metal cyanides,[3] and rare-earth metal-based ternary catalysts,[4] there are homogeneous catalysts based on various metals, especially zinc, chromium, and cobalt, with significant activities.[5] Coates reported that zinc β-diiminate complexes are loosely associated into dimers during copolymerization,[6] leading to the deliberate preparation of various bimetallic zinc catalysts.[7] Such a bimetallic mechanism, though homogeneous, became a useful alternative for heterogeneous zinc dicarboxylates,[8] leading to the rapid development of mononuclear chromium-[9] and cobalt[10]-salen catalysts. Moreover, cooperation in dinuclear Cr[11] and Co[12] salen complexes ultimately enhanced the catalytic activity compared with their corresponding monomeric analogs.

Recent interest has been focused on less toxic metals;[13] however, few well-defined dinuclear complexes of group 2 metals such as magnesium, particularly mixed metal systems of group 2 metals, as well as rare-earth metal polyhydrides and alkyls and amidos have been introduced as catalysts for the copolymerization of cyclohexene oxide (CHO) and CO_2. The highest turnover frequency (TOF) based on these group 2 and rare-earth metal complexes is 750 h^{-1}.[13k] Recently, Williams successfully isolated a rare example of a heterodinuclear complex having a magnesium atom and a zinc atom, which exhibited higher activity toward alternative copolymerization of CHO and CO_2 than either magnesium or zinc homodinuclear complexes.[14]

Metal complexes supported by macrocycles made of salen units recently attracted considerable attention in a wide range of applications, including metal ion recognition, magnetism, supramolecular assemblies, and nano-machines.[15] One of the most widely used macrocyclic multidentate ligands is the “tris(salen)” ligand that is composed of three salen moieties, although catalytic applications of such trimetalated macrocyclic tris(salene) complexes have never been reported. Herein, we report a new family of heterometallic catalysts comprised of a macrocyclic tris(Zn-salen) unit and a group 3 metal, among which the $Ce^{III}Zn$ complex exhibits high activity with a TOF over 370 h^{-1} for alternating copolymerization of CHO and CO_2. Furthermore, we provide the first example of the telomerization of polycarbonate using ammonium salts as chain transfer reagents to control the molecular weight while retaining the catalytic activity Various end-functionalized polycarbonates are selectively isolated in this catalytic system, and the key feature of this unique polycarbonate formation is the rapid ligand exchange of external carboxylate anions and coordinating polycarbonate anions on a precisely designed mixed-metal scaffold.

A complex $[LaZn_3(OAc)_3L^1]$ ($\mathbf{1_{La}}$), where L^1 is the hexa-anion of the macrocyclic tris(salen)-based ligand, was prepared by the template reaction of 1,4-diformyl-2,3-dihyroxylbenzene with 2,2-dimethyl-1,3-propanediamine in the presence of 1.0 equiv of $Zn(OAc)_2{\cdot}2H_2O$ and 1/3 equiv of $La(OAc)_3{\cdot}xH_2O$ (Scheme 1).[15e] To identify complexes that copolymerize CHO and CO_2, we first screened several diamines (1,3-diaminopropane, 1,2-diaminoethane, (1*R*,2*R*)-1,2-diphenylethylenediamine, and 1,2-bis(aminooxy)ethane) to prepare macrocyclic complexes. Complex $\mathbf{1_{La}}$ exhibited better solvability and the highest catalytic activity with high carbonate linkage. Thus, we focused our efforts on characterizing $\mathbf{1_{La}}$ and its derivatives (Scheme S1 and Table S1).

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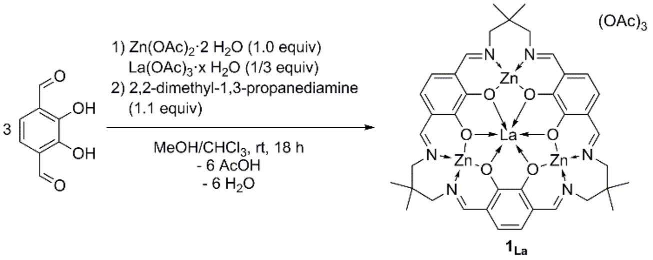
Scheme 1. Template Synthesis of $\mathbf{1_{La}}$.



Complex $\mathbf{1_{La}}$ was characterized by spectroscopic methods and combustion analysis. The ^{1}H NMR spectrum in methanol-d_4 at 30 °C displayed five singlets at δ 8.31 (s, 6H, N=C*H*), 6.62 (s, 6H, *Ar*), 3.81 (s, 12H, =NC*H*$_2$-), 1.81 (s, 9H, C*H*$_3$CO$_2$), and 1.08 (s, 18H, CH$_2$C(C*H*$_3$)$_2$CH$_2$), suggesting a C_3 symmetric structure in solution. Three acetate anions were observed as a magnetically equivalent singlet at room temperature, and the fluxional intramolecular exchange of the three acetate ligands was rapid even at –90 °C (Figure S1)[16a,17], though the different coordination modes of the three acetates were clarified by a single crystal structure determination of $\mathbf{1_{La}}$ (*vide infra*).

Another notable feature of $\mathbf{1_{La}}$ was the rapid exchange between the coordinated acetates and outer sphere acetate anions: the singlet signal at δ 1.85 due to the three acetate ligands shifted to δ 1.88 (s, 12H, OCOC*H*$_3$) upon adding 1 equiv of [^{n}Bu$_4$N][OAc] (δ 1.90), and, furthermore, increasing amounts of [^{n}Bu$_4$N][OAc] up to 10 equiv induced the saturation of chemical shift at δ 1.89 (Figure S2). On the basis of the Job-Plot, $\mathbf{1_{La}}$ and [^{n}Bu$_4$N][OAc] formed a 1:1 anionic complex in methanol-d_4, and the binding constant was estimated to be 373 M^{-1} (Figures S3 and S4).[18,19] Under saturated conditions, the intramolecular exchange was still too rapid because the singlet signal at δ 1.88 was not coalesced even at –90 °C (Figures S5). Accordingly, we proposed an equilibrium mixture of possible structures in Figure 1.[16b,17]

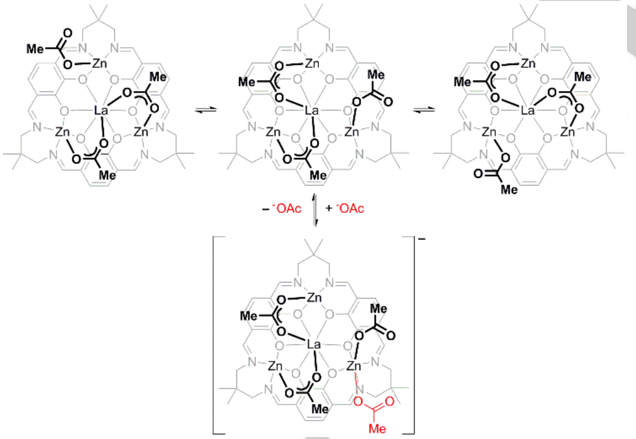


Figure 1. Intramolecular and intermolecular rapid exchange of acetate anions.

Such a rapid exchange between inner acetates and outer acetates prompted us to compare the effects of different anions. Thus, we prepared nitrate and triflate analogs by treating La(NO$_3$)$_3$·6H$_2$O with Zn(OAc)$_2$ and La(OTf)$_3$·xH$_2$O with Zn(OAc)$_2$ as the sources of the lanthanum and zinc ion. The corresponding complexes [LaZn$_3$(NO$_3$)$_2$L^1](NO$_3$) ($\mathbf{2_{La}}$) and [LaZn$_3$(OTf)$_2$(OAc)L^1] ($\mathbf{3_{La}}$) were obtained in moderate yields. The ^{1}H NMR spectral patterns of $\mathbf{2_{La}}$ and $\mathbf{3_{La}}$ were quite similar to those of the acetate complex $\mathbf{1_{La}}$ except for the singlet due to the acetate ligands.

Figures 2(a) and 2(b) show the solid state structures of $\mathbf{1_{La}}$ and $\mathbf{2_{La}}$, respectively. Complex $\mathbf{1_{La}}$ has two kinds of acetate ligands: two of the three acetates form a bridge between a zinc atom and a lanthanum atom, and the other is η^1-mode bound to zinc. In the case of $\mathbf{2_{La}}$, the lanthanum atom has two κ^2-nitrate ligands, one nitrate exists as an anion, and each zinc atom has one methanol as a ligand.

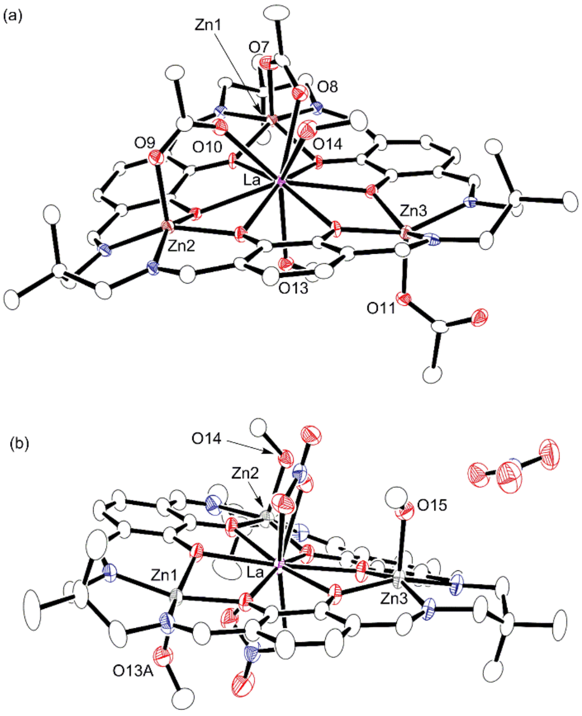
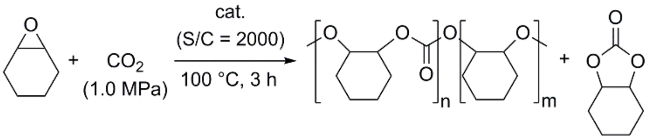


Figure 2. Molecular structures of $\mathbf{1_{La}}$ (a) and $\mathbf{2_{La}}$ (b). All hydrogen atoms and solvent molecule are omitted for clarity.

With three lanthanum complexes having different anions, $\mathbf{1_{La}}$, $\mathbf{2_{La}}$, and $\mathbf{3_{La}}$, in hand, we conducted the copolymerization of CHO with CO$_2$ and the results are shown in Table 1. The nature of the anionic ligand was critical to achieve superior catalytic performance. Among the lanthanum complexes tested, acetate complex $\mathbf{1_{La}}$ was the best catalyst for copolymerization in terms of the high catalytic activity and perfect carbonate linkage (>99%). In sharp contrast, nitrate complex $\mathbf{2_{La}}$ resulted in only a trace amount of the polymer, and triflate complex $\mathbf{3_{La}}$ showed high catalytic activity for polyether formation with only 1% carbonate linkage.

Table 1. Catalytic activity and selectivity of $\mathbf{LaZn_3X_3L^1}$.



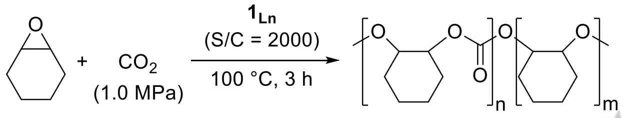
Entry	Cat.	TOF[a] /h^{-1}	Carbonate linkage[b] /%	Cyclic carbonate[c] /%
1	$\mathbf{1_{La}}$	230	> 99	< 1
2	$\mathbf{2_{La}}$	trace	-	-

3	**3**$_{\mathbf{La}}$	413	1	< 1

[a] Turn Over Frequency = mole [CHO] consumed per mole catalyst per hour. [b] Determined by the relative integrals of the ^{1}H NMR resonances at δ = 3.45 (polyether) and δ = 4.65 ppm (polycarbonate). [c] Determined by ^{1}H NMR spectroscopy.

Because acetate complex **1**$_{\mathbf{La}}$ showed superior catalytic performance with high carbonate linkage (>99%), we examined variations of **1**$_{\mathbf{Ln}}$ using lanthanide elements for co-polymerization, and the results are summarized in Table 2. Complexes of larger lanthanides, such as La, Ce, Pr, and Nd, resulted in higher catalytic activities compared with middle or late lanthanide elements with very high carbonate linkage and a narrow molecular weight distribution retained. This suggests that living polymerization proceeded even though these complexes have three acetate coordination sites that act as initiation sites. Complex **1**$_{\mathbf{Ce}}$ showed high catalytic activity with high carbonate linkage even under lower CO$_2$ pressure (Entries 3 and 4). As a result, we selected complex **1**$_{\mathbf{Ce}}$ as the optimal catalyst precursor. The crystal structure of **1**$_{\mathbf{Ce}}$ is shown in Figure S35.[19]

Table 2. Catalytic activity and selectivity of **1**$_{\mathbf{Ln}}$.



Entry	Ln	TOF[a] /h^{-1}	Carbonate linkage[b] /%	M_n[c] /g·mol^{-1}	PDI[c][d]
1	La	230	99	10000	1.2
2	Ce	370	> 99	14000	1.3
3[e]	Ce	330	> 99	14000	1.2
4[e]	Ce	300	> 99	15000	1.2
5	Pr	310	> 99	14000	1.3
6	Nd	320	> 99	18000	1.2
7	Sm	290	> 99	21000	1.2
8	Eu	250	> 99	11000	1.2
9	Gd	200	> 99	11000	1.2
10	Dy	100	98	6600	1.2

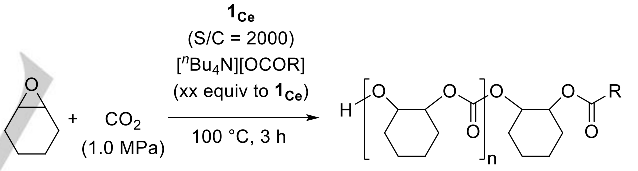
[a] Turn Over Frequency = mole [CHO] consumed per mole catalyst per hour. [b] Determined by the relative integrals of the ^{1}H NMR resonances at δ = 3.45 (polyether) and δ = 4.65 ppm (polycarbonate). [c] Determined by GPC in THF, using polystyrene standards as the calibrant. [d] Bimodal molecular weight distribution in GPC was observed. [e] The pressure of CO$_2$ was 0.6 MPa. [e] The pressure of CO$_2$ was 0.3 MPa.

Additive effects of ammonium carboxylates.

We investigated the telomerization of polycarbonate by adding excess amounts of carboxylate anions based on the observed fluxional behavior of acetates in an intramolecular and intermolecular manner (Table 3). Alternative copolymerization of CHO and CO$_2$ in the presence of [^{n}Bu$_4$N][OAc] (1.0 equiv to **1**$_{\mathbf{Ce}}$) gave a lower molecular weight polymer (Entry 1). By adding larger amounts of [^{n}Bu$_4$N][OAc] (2.0, 5.0, and 10.0 equiv to **1**$_{\mathbf{Ce}}$), the molecular weight of the polycarbonate gradually decreased (Entries 2—4). The catalytic activity was reduced by 20.0 equiv of [^{n}Bu$_4$N][OAc] and the oligomer was afforded (Entry 5). These polymers were characterized by ^{1}H NMR spectroscopic analysis and MALDI-TOF-MS, and determined to be bimodal due to two kinds of polymers, one of which had two hydroxyl groups at both terminals (HO-/HO-terminated polymer) due to water contamination,[13c] and the other of which had one acetate terminal group and one hydroxy terminal group (AcO-/HO-terminated polymer).[19] In the case of 10.0 equiv of [^{n}Bu$_4$N][OCO^{t}Bu], we obtained a mixture of ^{t}BuCOO-/HO-terminated and HO-/HO-terminated polymers along with a trace amount of AcO-/HO-terminated polymer (Entry 6).

Moreover, the addition of various ammonium benzoates afforded ArCOO-/HO-terminated polymers with the corresponding benzoate moiety as one terminal group and a hydroxyl group as the other terminal group, along with contamination of the AcO-/HO-terminated polymer (Entries 7—10), suggesting that almost all acetate ligands were readily replaced by the added ammonium benzoates. To the best of our knowledge, this is the first example of the telomerization of polycarbonate by adding excess amounts of carboxylate anions, although additive effects of H$_2$O, HNR$_2$, HSR, and HOSiR$_3$ were investigated,[20] and additive effects of ammonium salts were observed for catalyst systems of salen-type metal complexes for copolymerization to improve catalytic activity and control selectivity, as well as the formation of cyclic carbonate from epoxides and CO$_2$.[10b-i,21]

Table 3. Telomerization to give polycarbonates.

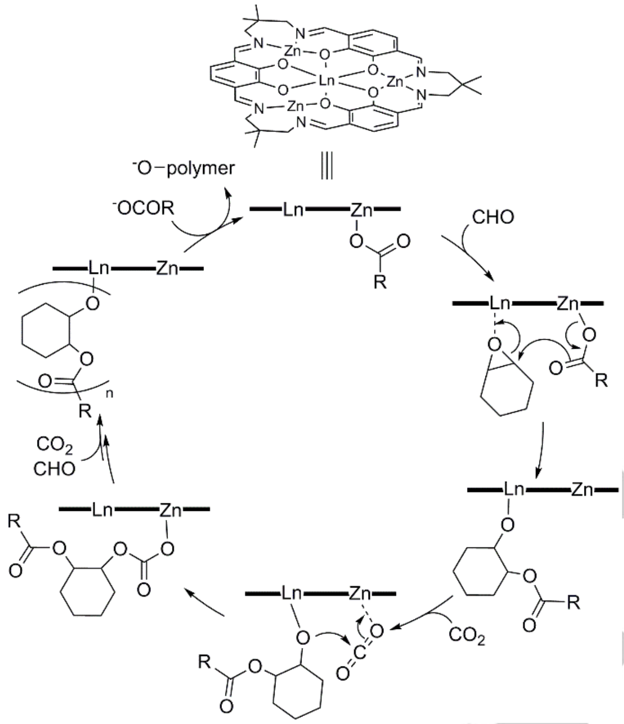


Entry	R	[^{n}Bu$_4$N][OAc] (equiv to **1**$_{\mathbf{Ce}}$)	TOF[a] /h^{-1}	M_n[b] /g·mol^{-1}	PDI[b][c]
1	CH$_3$	1.0	360	11000	1.3
2	CH$_3$	2.0	300	9300	1.2
3	CH$_3$	5.0	290	6900	1.2
4	CH$_3$	10.0	350	4300	1.2
5	CH$_3$	20.0	180	1800	1.2
6	^{t}Bu	10.0	250	4000	1.2
7	Ph	10.0	270	5500	1.2
8	4-ClC$_6$H$_4$	10.0	310	6500	1.2
9	4-BrC$_6$H$_4$	10.0	300	4800	1.2
10	4-vinylC$_6$H$_4$	10.0	390	5400	1.2

[a] Turn Over Frequency = mole [CHO] consumed per mole catalyst per hour.
[b] Determined by GPC in THF, using polystyrene standards as the calibrant.
[c] Bimodal molecular weight distribution in GPC was observed.

We propose a reaction mechanism of alternative copolymerization of CHO and CO$_2$ catalyzed by complex **1**$_{\mathbf{Ln}}$ based on the above controlled experiments and dynamic behavior of the acetate ligands (Scheme 2). As an initiation of the polymerization, the η^{1}-acetate bound to the zinc atom attacks CHO activated by the proximate lanthanide element to generate the Ln-alkoxide species. At the propagation stage, the alkoxide bound to the lanthanide element reacts with CO$_2$ activated by the zinc atom, where the Zn(II) center in macrocycles favors binding with CO_2,[6,22] resulting in the formation of carbonate bound to the zinc center, which further attacks the activated CHO on the lanthanide element. Overall, the alternating polymerization proceeded in a living manner, even under low CO_2 pressure. After the propagation reaction, chain transfer reaction with added ammonium carboxylates proceeded to regenerate the η^1-carboxylate initiator along with the corresponding polymer with an ammonium alkoxide terminal group as a key telomerization step.

Scheme 2. A plausible reaction mechanism.



In conclusion, we demonstrated that heterometallic complexes composed of trimetallated macrocycles and one lanthanide element became a new family of structurally characterized catalysts for the copolymerization of CHO and CO_2 with a high carbonate linkage (complete alternating copolymerization) and narrow PDI (living nature). To our surprise, the acetate anions were flexible over not only an intramolecular rapid exchange, but also an intermolecular exchange with outer sphere ammonium acetate or benzoates, resulting in the control of molecular weight as a new type of telomerization and incorporation of carboxylate derivatives as the initiation group of the polymers. The development of homogeneous heterometallic complexes as supramolecular catalysts is ongoing in our laboratory.

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Keywords: Macrocycles • Lanthanide • Zinc • Copolymerization • Telomerization

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[16] a) Figure 1 shoews three possible neutral species where two of three acetates bridge between a zinc atom and a lanthanum atom, and the other is η^1-mode bound to zinc. In the solution phase, *uuu*- and *uud*-isomer were indistinctive, thus we described only *uuu*-isomer. b) The structure of anionic complex, which we proposed, a zinc atom has two η^1-acetate ligands both of up and down side such structure was reported in Co-salen complex. See reference 10e

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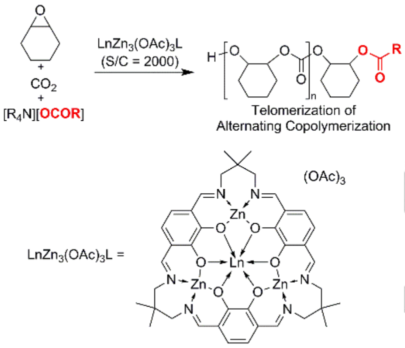
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

A new family of homogeneous heterometallic complexes based on trizincated macrocycle trisaloph and rare earth metals showed high catalytic activity for the alternating copolymerization of cyclohexene oxide and CO_2 with high proportion of carbonate repeat units. Carboxylate anion of ammonium salts acted as initiator to proceed telomerization of polycarbonate which have corresponding carboxylates as the initiation group.



Haruki Nagae, Ryota Aoki, Shin-nosuke Akutagawa, Julian Kleemann, Risa Tagawa, Tobias Schindler, Gyeongshin Choi, Thomas P- Spaniol, Hayato Tsurugi, Jun Okuda, and Kazushi Mashima

Lanthanide Complexes supported by a Trizinc-crown Ether as catalysts for Alternating Copolymerization of Epoxide and CO_2: Telomerization Controlled by Carboxylate Anions