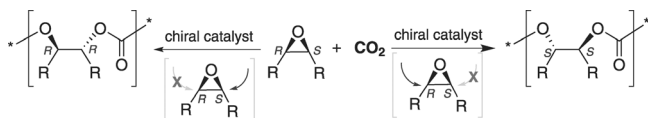


# Asymmetric Copolymerization of CO<sub>2</sub> with *meso*-Epoxides Mediated by Dinuclear Cobalt(III) Complexes: Unprecedented Enantioselectivity and Activity\*\*

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The desymmetrization of *meso*-epoxides by nucleophilic ring-opening using chiral catalysts or reagents is a valuable strategy for the synthesis of enantiomerically enriched compounds with two contiguous stereogenic centers.<sup>[1]</sup> When such a powerful synthetic strategy is applied to the alternating copolymerization of CO<sub>2</sub> with *meso*-epoxides, optically active polycarbonates with chiral (*R,R*)- or (*S,S*)-*trans*-1,2-diol units in the main chain can be produced, owing to the configurational inversion at one of the two chiral centers of the *meso*-epoxides that are incorporated into the copolymer (Scheme 1). The first attempt of asymmetric copolymerization of CO<sub>2</sub> with cyclohexene oxide (CHO) was disclosed by



**Scheme 1.** Asymmetric copolymerization of CO<sub>2</sub> with *meso*-epoxides.

Nozaki et al. using a 1:1 Et<sub>2</sub>Zn/(*S*)- $\alpha,\alpha$ -diphenyl(pyrrolidin-2-yl)methanol mixture as catalyst, producing the corresponding polycarbonates with moderate enantioselectivity.<sup>[2]</sup> Soon thereafter, the Coates research group reported the use of chiral hybrid imineoxazoline zinc-based catalysts for this reaction, which showed similar enantioselectivity but higher activity and controlled molecular weight.<sup>[3]</sup> Further mechanistic studies suggested that a dimeric zinc complex might be the active species.<sup>[4]</sup> Interestingly, the CO<sub>2</sub>/CHO coupling mediated by an enantiopure dinuclear zinc complex developed by Ding provided the copolymer product with only 18 % enantioselectivity.<sup>[5]</sup> A moderate enantioselectivity (60–80 % *ee*) was also observed in the copolymerization of CO<sub>2</sub> with *meso*-epoxides catalyzed by optically active dinuclear alumi-

num complexes of  $\beta$ -ketoiminate or aminoalkoxide, in conjunction with a bulky Lewis base as catalyst activator.<sup>[6]</sup>

Recently we reported the synthesis of highly isotactic poly(cyclohexene carbonate) composed of 1,2-cyclohexanediol units with 96 % *ee* using a binary catalyst system that consisted of an unsymmetrical chiral SalenCo<sup>III</sup> complex and bis(triphenylphosphine)iminium chloride (PPNCl), but the rigorous reaction conditions, such as a low temperature of –25 °C and the use of a large amount of chiral induction agent, were prerequisites for obtaining optically active copolymer with low molecular weight in a very low rate (less than 3 h<sup>–1</sup>).<sup>[7]</sup> In addition, this binary catalyst system was found to be inactive for the coupling of CO<sub>2</sub> with cyclopentene oxide (CPO; a less reactive epoxide). In fact, a significant decrease in reactivity was also mentioned in the reported zinc-based catalyst systems.<sup>[2,3]</sup> As a consequence, the synthesis of highly stereoregular CO<sub>2</sub> copolymers from CPO is challenging, and thus the development of a catalyst for this enantioselective transformation became a primary goal of our research.

Herein, we report a chiral catalyst system based on enantiopure dinuclear Co<sup>III</sup> complexes **1** with a rigid bridging biphenyl linker, which exhibits excellent activity, unprecedented enantioselectivity, and molecular-weight control for the alternating copolymerization of CO<sub>2</sub> with *meso*-epoxides (both CPO and CHO) under mild reaction conditions. Before, Jacobsen and co-workers demonstrated that the construction of covalently linked dimeric complexes resulted in an enhanced catalytic activity in the SalenCr<sup>III</sup>Cl-catalyzed asymmetric ring opening of CPO using TMSN<sub>3</sub>.<sup>[8]</sup> Also, in the copolymerization of epoxides with CO<sub>2</sub> using coordination polymerization catalysis, the bimetallic synergistic effect was frequently observed.<sup>[4–6,9–11]</sup>

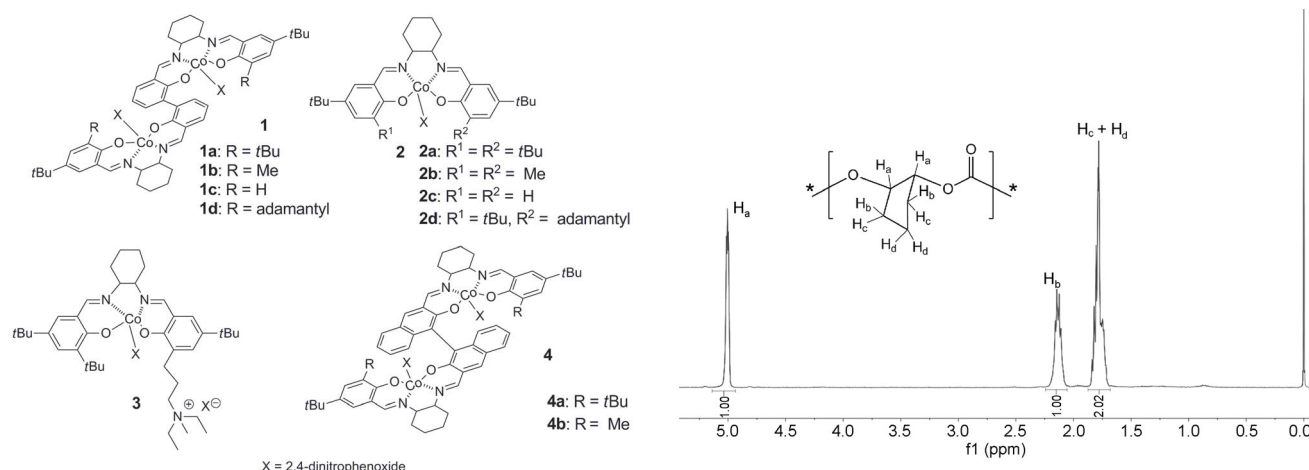
Indeed, our initial study mainly focused on enantiomerically pure mononuclear Co<sup>III</sup> complexes **2** and **3** with an inter- or intramolecular nucleophilic cocatalyst for CO<sub>2</sub>/CPO copolymerization, stimulated by the success with these chiral Co<sup>III</sup> complexes in catalyzing alternating copolymerization of CO<sub>2</sub> with aliphatic epoxides.<sup>[12–14]</sup> To our disappointment, the formation rate of CO<sub>2</sub> copolymer is significantly lower than that of propylene oxide or cyclohexene oxide copolymers when using the same catalyst systems.<sup>[12b,c]</sup> Moreover, the enantioselectivity of the resultant copolymer is also not satisfactory (Table 1, entries 1 and 2, and Table S1 in the Supporting Information).

We discovered that enantiopure complexes (*S,S,S,S*)-**1a**, **1b**, and **1c** alone could operate at high efficiency in catalyzing CO<sub>2</sub>/CPO copolymerization, with turnover frequencies (TOF) of about 230 h<sup>–1</sup> at ambient temperature. The resultant

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**Figure 1.**  $^1\text{H}$  NMR spectrum of a representative sample of poly(cyclopentene carbonate) in  $\text{CDCl}_3$ .

copolymers show moderate enantioselectivities of 72–86 % (Table 1, entries 3–5), but possess perfectly alternating nature with >99 % carbonate unit content (Figure 1). Notably, the use of **1a**, **1b**, or **1c** with an *S,S,S,S* configuration predominantly provides the product with *S,S* configuration. The result is distinct from the binary or bifunctional catalyst systems based on complex (*S,S*)-**2** or (*S,S*)-**3**, with which  $\text{CO}_2$ /CPO copolymerization mainly afforded the copolymers with *R,R* configuration (Table 1, entries 1 and 2). The screening results revealed that the steric hindrance of the phenolate

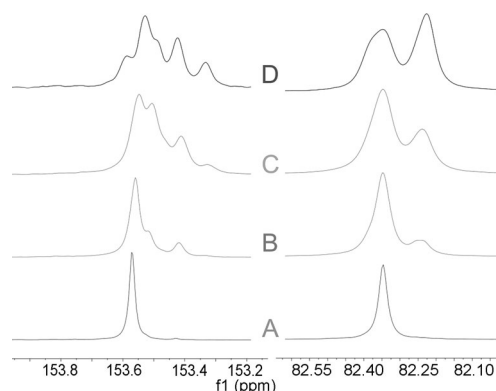
*ortho* substituents strongly influenced the catalytic activity and product enantioselectivity. The bulky substituents on the aromatic rings were not the best choice in this study. For example, dinuclear complex **1d** with bulky adamantyl groups on the phenolate *ortho* position showed a low activity of  $11 \text{ h}^{-1}$  and poor enantioselectivity of 45 % *ee* in catalyzing this reaction under the same conditions (Table 1, entry 6).

**Table 1:** Asymmetric copolymerization of  $\text{CO}_2$  with cyclopentene oxide mediated by enantiopure  $\text{Co}^{\text{III}}$  complexes.<sup>[a]</sup>

Entry	Catalyst	CPO/ $\text{Co}^{\text{III}}$ complex/PPNX <sup>[b]</sup>	$p(\text{CO}_2)$ [MPa]	$t$ [h]	TOF [ $\text{h}^{-1}$ ] <sup>[c]</sup>	Selectivity [%] <sup>[d]</sup>	$M_n$ <sup>[e]</sup> [ $\text{kg mol}^{-1}$ ]	PDI <sup>[e]</sup>	<i>ee</i> [%] <sup>[f]</sup>	Specific rotation [ $^\circ$ ] <sup>[g]</sup>
1	( <i>S,S</i> )- <b>2a</b> /PPNX	500:1:1	2	48	3	93	11.8	1.18	31( <i>R,R</i> )	18(–)
2	( <i>S,S</i> )- <b>3</b>	500:1:0	2	48	3	>99	14.0	1.21	32( <i>R,R</i> )	20(–)
3	( <i>S,S,S,S</i> )- <b>1a</b>	1000:1:0	2	1	235	>99	36.5	1.27	72( <i>S,S</i> )	40(+)
4	( <i>S,S,S,S</i> )- <b>1b</b>	1000:1:0	2	1	225	>99	34.2	1.26	85( <i>S,S</i> )	51(+)
5	( <i>S,S,S,S</i> )- <b>1c</b>	1000:1:0	2	1	235	>99	35.9	1.25	86( <i>S,S</i> )	51(+)
6	( <i>S,S,S,S</i> )- <b>1d</b>	1000:1:0	2	24	11	>99	18.6	1.21	45( <i>S,S</i> )	26(+)
7	( <i>S,S,S,S</i> )- <b>1a</b> /PPNX	1000:1:2	2	2	191	>99	35.0	1.28	81( <i>S,S</i> )	46(+)
8	( <i>S,S,S,S</i> )- <b>1b</b> /PPNX	1000:1:2	2	2	199	>99	29.8	1.24	>99( <i>S,S</i> )	58(+)
9	( <i>S,S,S,S</i> )- <b>1c</b> /PPNX	1000:1:2	2	2	201	>99	31.7	1.26	>99( <i>S,S</i> )	58(+)
10	( <i>S,S,S,S</i> )- <b>1d</b> /PPNX	1000:1:2	2	24	10	>99	15.0	1.27	51( <i>S,S</i> )	30(+)
11	( <i>S,S,S,S</i> )- <b>1b</b> /PPNX	1000:1:2	0.1	8	42	>99	20.2	1.41	96( <i>S,S</i> )	56(+)
12	( <i>S,S,S,S</i> )- <b>1b</b> /PPNX	1000:1:2	0.6	2	128	>99	23.8	1.25	97( <i>S,S</i> )	57(+)
13 <sup>[h]</sup>	( <i>S,S,S,S</i> )- <b>1b</b> /PPNX	1000:1:2	2	0.5	647	>99	22.2	1.40	88( <i>S,S</i> )	52(+)
14 <sup>[i]</sup>	( <i>S,S,S,S</i> )- <b>1b</b> /PPNX	1000:1:2	2	6	167	>99	73.4	1.28	>99( <i>S,S</i> )	58(+)
15	( <i>S,S,S,S</i> )- <b>1b</b> /PPNX	2000:1:2	2	6	137	>99	30.9	1.28	>99( <i>S,S</i> )	58(+)
16 <sup>[i]</sup>	( <i>S,S,S,S</i> )- <b>1b</b> /PPNX	2000:1:2	2	18	111	>99	107.9	1.36	>99( <i>S,S</i> )	58(+)
17	( <i>R,R,S,R,R</i> )- <b>4a</b> /PPNX	1000:1:2	2	48	6	94	7.5	1.32	25( <i>R,R</i> )	15(–)
18	( <i>S,S,S,S,S</i> )- <b>4a</b> /PPNX	1000:1:2	2	48	4	93	5.6	1.21	33( <i>R,R</i> )	20(–)
19	( <i>R,R,S,R,R</i> )- <b>4b</b> /PPNX	1000:1:2	2	48	7	95	8.7	1.28	20( <i>R,R</i> )	10(–)

[a] The reaction was performed in neat CPO (2.6 mL, 30 mmol) in a 20 mL autoclave at 25 °C. X = 2,4-dinitrophenoxide. The carbonate linkages of all the resulting polycarbonates are >99 % based on  $^1\text{H}$  NMR spectroscopy. [b] Molar ratio. [c] Turnover frequency (TOF) = mol of product (polycarbonates)/mol of catalyst per hour. [d] Selectivity for polycarbonates over cyclic carbonate, determined by using  $^1\text{H}$  NMR spectroscopy. [e] Determined by using gel permeation chromatography in THF, calibrated with polystyrene. [f] Hydrolyzing the polymer, derivatizing of the resultant diol using benzoyl chloride, and then determining the *ee* of the dibenzoate by chiral HPLC. [g] Specific rotation of the polymers was determined in chloroform at 20 °C ( $c=1$ ) by using a polarimeter. [h] The reaction was carried out at 50 °C. [i] The reaction was carried out in toluene solution CPO/toluene = 1:2 (volume ratio).

The addition of a nucleophilic cocatalyst significantly improved the product enantioselectivity, accompanied with a slight decrease in catalytic activity (Table 1, entries 7–10).<sup>[15]</sup> Dinuclear cobalt complex **1b** or **1c** in conjunction with PPNX (X = 2,4-dinitrophenoxide) was used as catalyst for CO<sub>2</sub>/CPO copolymerization, affording the polymer product with an unprecedented enantioselectivity of 99% *ee* at 25 °C. The polymer exhibited a specific rotation value  $[\alpha]_D^{20} = +58$  (*c* = 1 in CHCl<sub>3</sub>). Although we have not given the accurate assignment of the microstructure of poly(cyclopentene carbonate), significant differences in both the carbonyl and methine region between the atactic and highly isotactic copolymers are easily identified by <sup>13</sup>C NMR spectroscopy (Figure 2).



**Figure 2.** The carbonyl (left) and methine (right) region of <sup>13</sup>C NMR spectra of the polycarbonates resulted from CO<sub>2</sub>/CPO copolymerization catalyzed by A) **1c**, *ee* > 99%; B) **1a**, *ee* = 81%; C) **1d**, *ee* = 51%; D) racemic **2a**, *ee* = 0% in the presence of PPNX (X = 2,4-dinitrophenoxide).

Notably, the catalyst system could operate at high efficiency with CO<sub>2</sub> even at atmospheric pressure, with a TOF of 42 h<sup>−1</sup> and an enantioselectivity of 96% at ambient temperature (Table 1, entry 11). An increase in reaction temperature resulted in an enhancement of the rate, but has a negative effect on asymmetric induction. When the dinuclear cobalt catalyst system was used at 50 °C, a completely alternating copolymer with an enantioselectivity of 88% *ee* with *S,S* configuration was obtained (Table 1, entry 13). When the CPO/catalyst ratio was increased to 2000, no obvious change in catalyst activity and enantioselectivity was observed (Table 1, entry 15). Especially, with the use of toluene as an organic solvent, complete conversion was achieved in the copolymerization performed at 25 °C within prolonged time, affording the polycarbonate with a high molecular weight (*M*<sub>n</sub> = 107 900; Table 1, entry 16, and Figure S9 in the Supporting Information).

Notably, a binary catalyst system consisting of a dinuclear cobalt complex **4** with a chiral binaphthol linker and PPNOAc was shown to be an effective catalyst for highly enantioselective homopolymerization of terminal epoxides through a kinetic resolution process.<sup>[16]</sup> The dinuclear Co<sup>III</sup> complex **4** was also tested for the asymmetric copolymerization of CO<sub>2</sub>

with CPO (Table 1, entries 17–19). Unfortunately, the binary catalyst systems based on complex **4a** or **4b** showed a very low activity, affording the copolymers with poor enantioselectivity (20–33% *ee*). The difference in linker (binaphthol versus biphenyl linker) resulting in the great discrepancy in both catalyst activity and product enantioselectivity was tentatively ascribed to the differences in the Co–Co distance and dihedral angle between the two Salen planes. Although much effort was placed in attempts to clarify the structure of these dinuclear Co<sup>III</sup> complexes, we failed to isolate their crystals. Fortunately, we obtained the X-ray crystal structure of a dinuclear Al<sup>III</sup> complex bridged with a biphenyl group and chlorine as axial group.<sup>[17]</sup> The complex displays an Al–Al distance of 7.89 Å and an *exo* phenyl–phenyl dihedral angle of 45.1°. In comparison to complex **4a** (chloride ion as axial group) with a Co–Co distance of 6.45 Å and an *endo* naphthyl–naphthyl dihedral angle of 79°,<sup>[16b]</sup> the dinuclear Al<sup>III</sup> complex has a wider metal–metal separation, consistent with the flexible nature of the biphenyl linker. Therefore, we speculate that the long Co–Co separation in complex **1a** might be beneficial for copolymerizing CO<sub>2</sub> with epoxides.

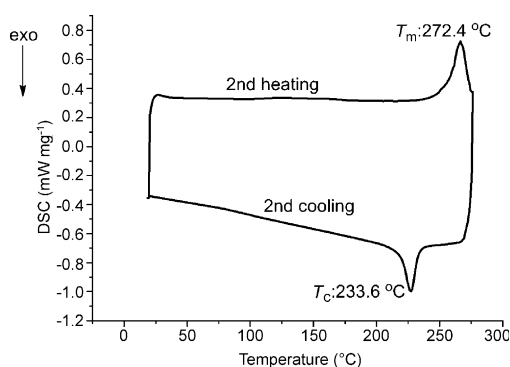
The same catalyst systems were also tested for the asymmetric copolymerization of CO<sub>2</sub> with cyclohexene oxide. The enantiopure complexes (*S,S,S,S*)-**1a**, **1b**, and **1c** alone could also operate at high efficiency in catalyzing this asymmetric copolymerization with TOFs of about 200 h<sup>−1</sup> at 25 °C (Table 2, entries 1–3). Moreover, both catalytic activity and copolymer enantioselectivity were dramatically enhanced by adding PPNX (X = 2,4-dinitrophenoxide) as cocatalyst, resulting in TOFs of about 1400 h<sup>−1</sup> (Table 2, entries 5–7).<sup>[18]</sup> The product enantioselectivity decreased with increasing size of the substituents in the phenolate *ortho* positions (*ee*: 81% > 77% > 47% > 12%; size: H < Me < *t*Bu < adamantyl) in the presence of PPNX (Table 2, entries 5–8). Notably, when the copolymerization proceeded at 0 °C and in the presence of the organic solvent toluene, the resultant poly(cyclohexene carbonate) possesses a highly enantiopurity up to 98% *ee* (Table 2, entry 10), with a specific rotation value  $[\alpha]_D^{20} = +26$  (*c* = 1 in CHCl<sub>3</sub>). <sup>13</sup>C NMR spectroscopy indicated that the copolymer had a perfectly isotactic structure (Figure S17 in the Supporting Information). The crystallization and melting behavior of the highly isotactic poly(cyclohexene carbonate) was studied by using DSC in a nitrogen flow (Figure 3). A quite sharp and high melting endothermic peak at 272.4 °C with  $\Delta H_m = 24.698$  J g<sup>−1</sup> and a crystallizing exothermic peak at 233.6 °C with  $\Delta H_c = -22.017$  J g<sup>−1</sup> were found. The value is significantly higher than that of our reported copolymer with 96% enantioselectivity and low molecular weight.<sup>[7]</sup> This result implies that the isotacticity of poly(cyclohexene carbonate) has a great effect on its crystallization performance.

In summary, we have developed an enantiopure dinuclear Co<sup>III</sup> catalyst with a rigid bridging biphenyl linker to induce complete desymmetrization copolymerization of *meso*-epoxides with CO<sub>2</sub> to give optically active polycarbonates. The combination of (*S,S,S,S*)-**1b** with a methyl group or (*S,S,S,S*)-**1c** without any substituents in the phenolate *ortho* positions and a nucleophilic cocatalyst PPNX (X = 2,4-dinitrophenoxide) was found to be more efficient in catalyzing this

**Table 2:** Asymmetric copolymerization of CO<sub>2</sub> with cyclohexene oxide mediated by enantiopure Co<sup>III</sup> complexes.<sup>[a]</sup>

<chem>C1CCC(CC1)O + CO2 &gt;&gt; [Chiral catalyst] *-[O-C6H10-C(=O)-O]_n*</chem>							
Entry	Catalyst	CHO/Co <sup>III</sup> complex/PPNX <sup>[b]</sup>	<i>t</i> [h]	TOF <sup>[c]</sup> [h <sup>-1</sup> ]	Mn <sup>[d]</sup> [kg mol <sup>-1</sup> ]	PD <sup>[d]</sup>	ee <sup>[e]</sup> [%]
1	(S,S,S,S)-1 a	1000:1:0	2	194	20.5	1.25	33
2	(S,S,S,S)-1 b	1000:1:0	2	189	19.7	1.19	67
3	(S,S,S,S)-1 c	1000:1:0	2	200	21.1	1.21	71
4	(S,S,S,S)-1 d	1000:1:0	10	17	8.5	1.11	5
5	(S,S,S,S)-1 a/PPNX	1000:1:2	0.25	1269	16.7	1.21	47
6	(S,S,S,S)-1 b/PPNX	1000:1:2	0.25	1356	11.5	1.18	77
7	(S,S,S,S)-1 c/PPNX	1000:1:2	0.25	1409	18.9	1.23	81
8	(S,S,S,S)-1 d/PPNX	1000:1:2	2	173	12.9	1.22	12
9	(S,S,S,S)-1 c/PPNX	5000:1:2	2	716	22.8	1.20	83
10 <sup>[f]</sup>	(S,S,S,S)-1 c/PPNX	1000:1:2	24	42	35.6	1.35	98

[a] The reaction was performed in neat CHO (3.0 mL, 30 mmol) in a 20 mL autoclave at 25 °C and a 2.0 MPa CO<sub>2</sub> pressure. X = 2,4-dinitrophenoxide. The polymer selectivity and carbonate linkages of the resulted polycarbonates are > 99% based on <sup>1</sup>H NMR spectroscopy. [b] Molar ratio. [c] Turnover frequency (TOF) = mol of product (polycarbonates)/mol of catalyst per hour. [d] Determined by using gel permeation chromatography in THF, calibrated with polystyrene. [e] Measured by hydrolyzing the polymer and analyzing the resulting diol by chiral GC, and the (S,S)-diol is the major enantiomer. [f] The reaction was carried out in toluene solution CHO/toluene = 1:2 (volume ratio) at 0 °C.



**Figure 3.** DSC thermograms of poly(cyclohexene carbonate) with 98% ee in second heating and cooling cycle. The sample was heated to 200 °C to crystallize.

asymmetric reaction, providing the copolymer with > 99% carbonate linkages and an enantioselectivity of up to 99% for S,S configuration. Further studies are focused on elucidating the catalytic mechanism and developing new dinuclear catalyst systems that exhibit higher activity and excellent enantioselectivity for the copolymerization of CO<sub>2</sub> with various epoxides under mild conditions.

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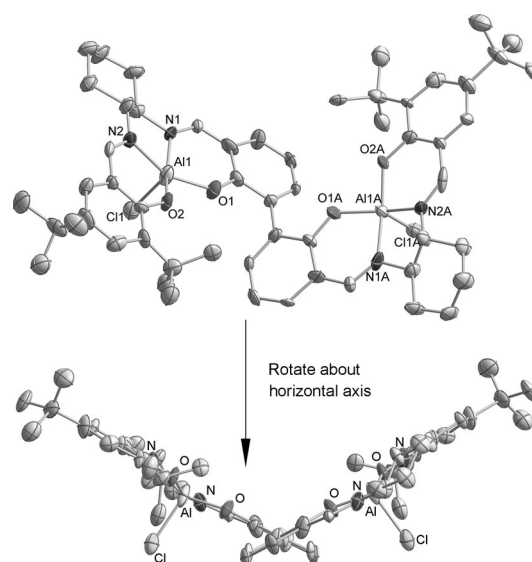
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- [15] Usually, the addition of a nucleophilic cocatalyst greatly increases the catalytic activity of both mono- and dinuclear  $\text{Co}^{\text{III}}$  complexes for  $\text{CO}_2$ /epoxide copolymerization (See Refs. [9a,12,13]). However, in comparison with **1a**, **1b**, or **1c** alone as catalyst, the presence of cocatalyst PPNX resulted in a slight decreases in catalytic activity for  $\text{CO}_2$ /CPO copolymerization, but great increases in activity for  $\text{CO}_2$ /CHO copolymerization. This indicates the different propensity of the two *meso*-epoxides during the copolymerization with  $\text{CO}_2$ .
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- [17] Since the X-ray structure of the mononuclear  $\text{SalenAl}^{\text{III}}\text{Cl}$  complex is similar with that of  $\text{SalenCo}^{\text{III}}\text{Cl}$  bearing a cyclohexane diamine backbone [see: a) D. J. Darensbourg, D. R. Billoreaux, *Inorg. Chem.* **2005**, *44*, 1433–1742; b) C. T. Cohen, C. M. Thomas, K. L. Peretti, E. B. Lobkovsky, G. W. Coates, *Dalton Trans.* **2006**, 237–249], we believed that the structure of dinuclear  $\text{SalenAl}^{\text{III}}\text{Cl}$  can reflect the structural information of the corresponding dinuclear  $\text{SalenCo}^{\text{III}}$  complex.



Molecular structure of dinuclear  $\text{SalenAl}^{\text{III}}\text{Cl}$  (hydrogen atoms and uncoordinated solvent omitted for clarity; carbon atoms are unlabeled). Thermal ellipsoids are at the 30% probability level. The complex displays an Al–Al distance of 7.89 Å and an *exo* phenyl–phenyl dihedral angle of 45.1°.

- [18] Notably, the use of other nucleophilic cocatalysts, such as simple  $n\text{Bu}_4\text{NCl}$ , could significantly improve the activity of the dinuclear  $\text{Co}^{\text{III}}$  catalyst. However, the copolymerization is very sensitive to water, so the avoidance of water or the decrease to a great extent in the reaction system is necessary for obtaining a high reaction rate and copolymers with highly molecular weight.