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PAPER

CO_2/ethylene oxide copolymerization and ligand variation for a highly active salen–cobalt(III) complex tethering 4 quaternary ammonium salts†

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A cobalt(III) complex (**1**) of a salcy-type ligand tethering 4 quaternary ammonium salts, which is thought to act as a highly active catalyst for CO_2/propylene oxide (PO) copolymerization, also shows high activity (TOF, 25 900 h^{-1}; TON, 518 000; 2.72 kg polymer per g cat) and selectivity (>98%) for CO_2/ethylene oxide (EO) copolymerization that results in high-molecular-weight polymers (M_n, 200 000–300 000) that have strictly alternating repeating units. The related cobalt(III) complexes **11–14** were prepared through variations of the ligand framework of **1** by replacing the *trans*-1,2-diaminocyclohexane unit with 2,2-dimethyl-1,3-propanediamine, *trans*-1,2-diaminocyclopentane, or 1,1′-binaphthyl-2,2′-diamine or by replacing the aldimine bond with ketimine. These ligand frameworks are thought to favour the formation of the *cis*-β configuration in complexation, and the formation of the *cis*-β configuration in **11–14** was confirmed through NMR studies or X-ray crystallographic studies of model complexes not bearing the quaternary ammonium salts. Complexes **11**, **13**, and **14**, which adopt the *cis*-β configuration even in DMSO did not show any activity for CO_2/PO copolymerization. Complex **12**, which was constructed with *trans*-1,2-diaminocyclopentane and fluctuated in DMSO between the coordination and de-coordination of the acetate ligand as observed for **1**, showed fairly high activity (TOF, 12 400 h^{-1}). This fluctuating behaviour may play a role in polymerization. However, complex **12** did not compete with **1** in terms of activity, selectivity, and the catalyst cost.

Introduction

Carbon dioxide/propylene oxide (CO_2/PO) copolymers, *i.e.*, poly(propylene carbonate) (PPC), are in an early stage of commercialization.[1–3] PPC is an attractive material not only because it is composed of 44% CO_2 by weight but also because it has some advantageous properties. Commodity polymers such as PVC and PS emit large amounts of toxic materials and tar when burning, which can cause injuries during fires, but PPC burns without emitting any toxic materials, and it may, thus, be utilized for formation of interior materials. It is adhesive toward cellulosic and metal substrates and is therefore suitable as a coating material. It displays good barrier properties for oxygen and water, making it suitable as food packaging material. One of its most fascinating properties is its biodegradability. Currently, the demand for biodegradable polymers is increasing. German companies such as Siemens and BASF have recently developed an alternative material to polystyrene-based acrylonitrile–butadiene–styrene (ABS) plastic made from a blend of polyhydroxybutyrate and PPC.

In spite of those merits, the commercialization of PPC has lagged because of the lack of efficient catalysts.[4–6] Heterogeneous zinc catalysts are capable of producing high-molecular-weight PPC (M_n > 100 000) with fairly high activity.[7] However, the rate of polymerization is not high, and the process thus requires a long polymerization time (>12 h) in a batch-type reactor. Furthermore, it is costly to remove the catalyst residue after polymerization. The catalyst residue should be thoroughly washed out to ensure resin stability. In the presence of the catalyst residue, the resin is easily degraded during thermal processing and even during storage at room temperature.[8] Thus, the initial commercialization using the heterogeneous zinc catalyst has been limited to small-scale processes for special applications such as sacrificial binders because of the high resin price.[9]

During the last decade, several studies have addressed the development of homogeneous catalysts,[10–13] and, eventually, a highly active catalyst (salcy–cobalt(III) complex tethering 4 quaternary ammonium salts) was reported in 2008.[14] The initially reported catalyst was modified by the exchange of 2,4-dinitrophenolate anions for nitrate to eliminate the safety concerns and reduce the cost in a large-scale preparation (**1** in eqn (1)).[15,16] The rate of polymerization using catalyst **1** was extraordinarily higher (turnover frequency (TOF) > 20 000 h^{-1}) in CO_2/PO

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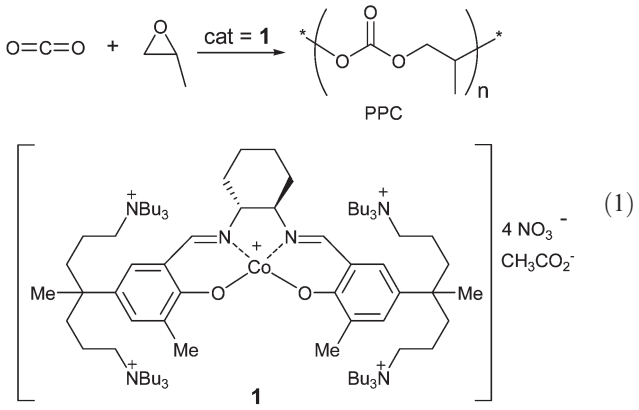
copolymerization than that of any other catalysts reported, and a high activity of up to 2.0 kg per g cat (57 kg per g Co: 32 900 TON) was attained by polymerization for just 2 h, thus permitting the polymerization process to proceed in a more efficient and continuous fashion. By employing **1** as a catalyst, a high-molecular-weight polymer (M_n up to 300 000) can be generated; moreover, the molecular weight can be controlled across a very large range of M_n 2000–600 000 by feeding a certain amount of chain transfer agents or chain extenders to the reaction.[17–19] Another advantage of **1** is that the catalyst can be efficiently removed simply by filtration through a thin pad of silica gel. After filtration, the resin contains a negligible amount of cobalt; hence, it is thermally stable up to 190 °C, which permits thermal processing without degradation and provides lasting mechanical stability.[20] The captured catalyst on the silica surface can be extracted for reuse, and **1** can be prepared in a large scale (100 kg per batch) with a minimal cost.[21,22] In this study, we report the CO_2/ethylene oxide (EO) copolymerization reactivity of **1** and some results related to our effort to find an efficient catalyst based on **1**.



(1)

Result and discussion

CO_2/EO copolymerization

CO_2 copolymerization using other epoxides, such as cyclohexene oxide, 1-hexene oxide, 1-butene oxide, styrene oxide, indene oxide, and epichlorohydrin, either alone or in combination with PO, has been previously reported.[23–27] However, the epoxides (except epichlorohydrin) are not currently produced on a bulk scale, and hence, polymers prepared using the epoxides are rarely relevant to commercialization on a large scale. One of the most attractive epoxides is EO, which is a bulk chemical that is annually produced on a scale of 15 million tons. Its production from ethylene using O_2 as an oxidant is more economical than PO, as the production of PO requires expensive oxidants such as H_2O_2 or Cl_2.

The CO_2/EO copolymer poly(ethylene carbonate) (PEC) is also a biodegradable material and has a slightly lower glass transition temperature (~20 °C) than PPC (~40 °C). However, studies on CO_2/EO copolymerization have rarely been reported. EO is a hazardous gas (b.p. 11 °C), and its handling requires specialized safety equipment. Its availability is also very limited in academic laboratories. We equipped an apparatus for CO_2/EO copolymerization in an industrial laboratory and investigated the reactivity of **1** in CO_2/EO copolymerization. As shown in Table 1, catalyst **1** functions equally well for both CO_2/EO copolymerization and CO_2/PO copolymerization. Extremely high activity of TOF up to 25 900 h^{-1} was achieved, corresponding to 2.72 kg polymer per g cat (entry 8). Polymers with high molecular weights of up to M_n = 272 000 were generated (entry 7), and a negligible amount of cyclic carbonate was formed during the polymerization (selectivity > 98%). In the ^1H NMR spectra, only 1 signal was observed at 4.4 ppm in $CDCl_3$, which indicates a perfect alternating structure that does not contain any ether linkage. The optimum polymerization temperature was approximately 70 °C in terms of activity and selectivity (entries 1–5), which was in accord with the optimum temperature for CO_2/PO copolymerization. As the CO_2 pressure increases, the activity increases gradually (entries 4, 6–8). At a low pressure of 20 bar, the selectivity decreases to 96%. After polymerization, the catalyst can be removed almost completely by passing the reaction mixture through a thin pad of silica gel to provide colourless polymers that contain a negligible amount of cobalt.

Cobalt(III) complexes of *cis*-β configuration

Recently, it has been reported that the capability to adopt the *cis*-β configuration (Fig. 1) may be related to high catalytic performance in CO_2/epoxide copolymerization.[28–30] Some ligand frameworks are known to be favourable for the formation of the *cis*-β configuration in complexation.[31] Typical examples are illustrated in Fig. 1. The *cis*-β configuration was found in a cobalt(III) acetate complex prepared from a flexible 1,3-diaminopropane-based compound such as **2**.[32,33] Compound **3** may favourably form the *cis*-β configuration because severe torsional strains are expected in the cyclopentane unit under the normal *trans* configuration. An X-ray crystallographic study of a single crystal of a ruthenium complex constructed with a binaphthyl Schiff base (**4** [R = Cl]) revealed the structure of the *cis*-β configuration.[34] Compound **5** constructed with 1,2-diaminocyclohexane and a 2′-hydroxyacetophenone derivative was also reported to be favourable for the formation of the *cis*-β configuration because of repulsion between the methyl and cyclohexane units. The *cis*-β structure of the $TiCl_2$ complex ligated by **5** (R═H) was revealed by X-ray crystallography.[35]

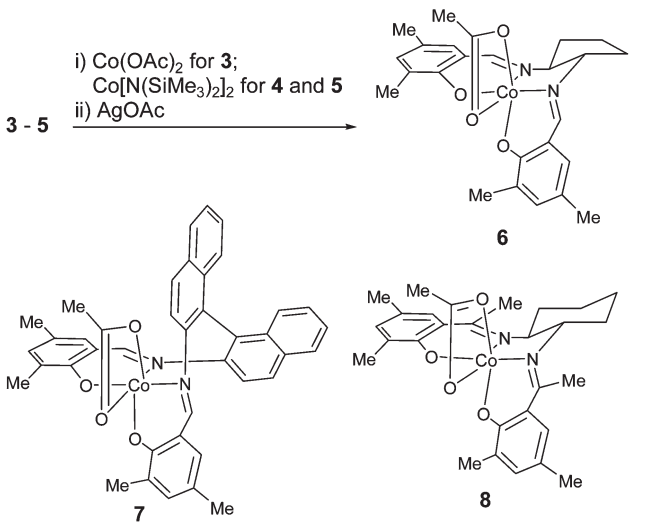
Cobalt complexes ligated by **3–5** have not been reported in the literature. Compound **3** (R = Me) can be easily constructed by reacting the corresponding salicylaldehyde and diamine in CH_2Cl_2 for 1 day. Compound **4** (R = Me) can be constructed by a condensation reaction in ethanol–acetic acid (7 : 1) at 60 °C. Construction of **5** (R = Me), which is prepared from a relatively less reactive ketone, requires more severe conditions (refluxing in 1-butanol for 2 days). Metallation of **3** (R = Me) was successfully performed by a well-established routine method: stirring the ligand with $Co(OAc)_2$ in CH_2Cl_2. The resulting cobalt(II) complex was converted to the corresponding cobalt(III) acetate complex **6** by using silver acetate as an oxidant (eqn (2)).[36] In the cases of **4** (R = Me) and **5** (R = Me), the corresponding cobalt complexes were not generated by the reaction with $Co(OAc)_2$. However, the desired cobalt(II) complexes were generated when the ligands were reacted with $Co[N(SiMe_3)_2]_2$ in

Table 1 CO_2/EO polymerization results[a]

Entry	T (°C)	P^b (bar)	Yield (g)	TOF (h^{-1})	M_n [c] × 10^{-3}	M_w/M_n	Selectivity[d] (%)
1	40	30	40	5040	121	1.45	98
2	50	30	50	6310	137	1.42	98
3	60	30	111	14 000	177	2.02	>99
4	70	30	146	18 400	225	2.50	>99
5	80	30	139	17 500	230	2.58	98
6	70	20	144	18 200	218	2.35	96
7	70	40	178	22 400	272	1.81	98
8	70	50	205	25 900	213	2.18	98

[a] Polymerization conditions: EO (800 g, 18.2 mol) [EO]/[**1**] = 400 000, **1** (0.075 g, 0.045 mmol), 2.0 h after initiation. [b] Total pressure of CO_2 and EO at the polymerization temperature. [c] Determined on GPC using a polystyrene standard in methylene chloride. [d] Selectivity of the polycarbonate over cyclic carbonate as determined by ^{1}H NMR spectroscopic analysis of the crude product.

CH_3CN overnight. The resulting cobalt(II) complexes were also converted to cobalt(III) acetate **7** and **8** by oxidation with silver acetate (eqn (2)).



(2)

In the ^{1}H NMR spectrum of **6** in CD_2Cl_2, very broad signals were observed, which did not provide any useful information about the binding mode, but the signal pattern in DMSO-d_6 was the same as that observed for the diaminocyclohexane analogue (Me-salcy)Co(III)OAc (Me-salcy = *N*,*N'*-bis(3,5-dimethylsalicylidene)-1,2-*trans*-diaminocyclohexane). Although these signals were broad, they could be assigned as 2 sets of signals in the ratio of approximately 4 : 1. The ratio was much higher than that observed for (Me-salcy)Co(III)OAc (10 : 1). In a previous report, this spectrum was assigned as an equilibrium between 2 species (eqn (3)).[28] The minor set was tentatively assigned to the symmetric structure of the acetate de-coordinated complex [(Me-salcy)Co(DMSO)$_2$]$^+$AcO$^-$ because it exhibited only 3 signals in the aromatic region. This assumption was further supported in this study by the addition of tetrabutylammonium acetate (0.5 equiv.), which resulted in the reduction of the minor set of signals. Six signals were observed in the aromatic region for the major set, indicating that the 2 salicylidene units were not equivalent. This observation can be assigned to (Me-salcy)Co(κ^2-OAc) of the *cis*-β configuration or to (Me-salcy)Co(κ^1-OAc)(DMSO) of the conventional *trans* configuration. The 2 salicylidene units

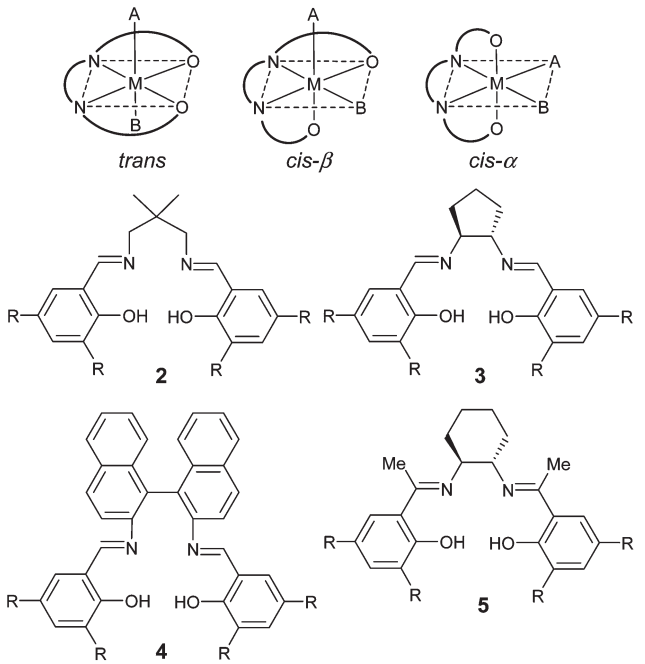
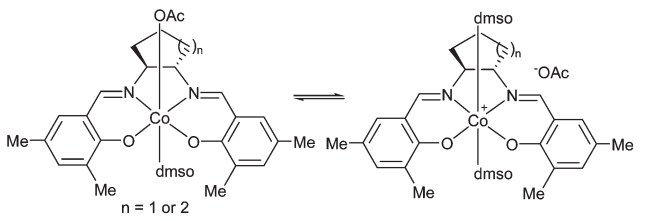


Fig. 1 Three possible configurations of the octahedral complexes formed by the tetradentate [NOON] ligand and the ligand frameworks favourable for the *cis*-β configuration.

are not magnetically equivalent, even in the *trans* configuration, for the complex constructed with a chiral diamine, whose axial sites are occupied by different ligands.[37] However, in the *trans* configuration, the signal separation for each corresponding salicylidene proton is not as severe as in that in the *cis*-β structure. The signal separation was small in the major set, and hence, it could preferably be assigned to (Me-salcy)Co(κ^1-OAc)(DMSO) of the conventional *trans* configuration.



(3)

In the ^{1}H and ^{13}C NMR spectra of **7** and **8**, sharp signals are observed in the normal range, indicating a diamagnetic low-spin state, and the signals can be assignable to the binding mode of the *cis*-β configuration. Some cobalt(III) complexes of the traditional *trans*-binding mode are in paramagnetic high-spin state, but all the cobalt(III) complexes adopting the *cis*-β configuration reported up to now are in diamagnetic low-spin state. In the ^{1}H NMR spectrum of **7** in CD_2Cl_2, 4 methyl signals were observed at 2.38, 2.25, 2.14, and 2.10 ppm, which indicated that the 2 dimethylsalicylidene units were not magnetically equivalent to each other. The signals in the aromatic region (8–6.5 ppm) also indicated that the 2 salicylidene units were not equivalent. The signal separation for each unit was fairly large, and 6 singlet signals were observed at 7.47, 7.01, 6.94, 6.82, 6.73, and 6.65 ppm for the salicylidene protons. Hence, the ^{1}H NMR spectrum of **7** could preferably be assigned to the *cis*-β configuration. In DMSO-d_6, complex **7** gave rise to a set of signals, which was contrary to the observation of 2 sets of signals for **6** and **1**. The signal pattern generated was the same as that observed in CD_2Cl_2, which implies the *cis*-β configuration, even in DMSO. In CD_3OD, the same signal pattern was observed, which indicates that **7** persistently adopts the *cis*-β configuration in CD_3OD.

In the ^{1}H NMR spectrum of **8** in CD_2Cl_2, both the halves of the ligand were also observed separately. Six singlet methyl signals were observed at 2.77, 2.62, 2.33, 2.25, 2.10, and 1.65 ppm. The 2 NC*H* signals were widely separated, as they were observed at 5.0 (very broad) and 3.60 ppm (broad triplet). These features strongly supported the *cis*-β configuration. In DMSO-d_6, a set of clear signals was observed with the same feature as observed in CD_2Cl_2, which implies that **8** also persistently adopts the *cis*-β configuration in DMSO.

X-ray crystallographic studies

When hexane is layer-diffused onto a brown solution of **6** in CH_2Cl_2 for several days, red crystals are deposited. The X-ray crystallographic studies of the single crystal revealed the structure of an unexpected cobalt(II) complex (Fig. 2). During the crystallization, the brown cobalt(III) complex was reduced to the corresponding cobalt(II) complex, which has a red colour. Most of the deposited crystals were red rather than brown, which indicates that **6** is readily reduced under the crystallization conditions. Such an easy reduction was also observed for the cobalt(III) acetate complex constructed from the *N*,*N*′-bis(3,5-dimethylsalicylidene)-1,2-*cis*-diaminocyclohexane.[28] In a single crystal, 2 enantiomers are randomly packed.

A solution of **7** in CD_3OD was evaporated to recover the sample that was redissolved in CH_2Cl_2. The solution in CH_2Cl_2 was layer-diffused with hexane to deposit brown crystals. The X-ray crystallographic studies revealed the structure of a cobalt(III) complex **7**, which was additionally coordinated by CD_3OD (Fig. 3). In the case of [NOON] cobalt(III) complexes, the *cis*-β configuration has been observed with a chelating ligand such as acetate, but in this binaphthyl Schiff base ligand, the *cis*-β configuration was preserved, even with monodentate ligands. In the *trans* configuration, the phenoxyimine ligand forms a stable coplanar structure with cobalt, but, in this *cis*-β configuration, both phenoxyimine ligands were found to be deviated from the formation of a strict plane with cobalt. The angle between the N═CCC–O plane and the N–Co–O plane was 32.70(6)° or 31.83(6)° for each phenoxyimine cobalt binding. The corresponding angles observed for the reduced cobalt(II) complex of **6** were 3.1(3)°. The angle between the 2 naphthyl rings was 65.13(7)°. The neutral methanol ligand was located opposite to the neutral imine ligand, whereas the anionic acetate ligand was opposite to the anionic phenoxy ligand. This binding trend was similar to that observed in the structure of (Me-salcy)Co(κ^2-OAc), where the Co-O(κ^2-OAc) distance opposite to the neutral imine ligand is longer (1.989(2) Å) than that opposite to the anionic phenoxy ligand (1.963(2) Å), whereas the C–O distance (1.265(6) Å) in the κ^2-OAc ligand is shorter for the oxygen opposite to the neutral imine ligand and is preferably assignable as a carbonyl oxygen.[28]

When hexane was layer-diffused onto a solution of **8** in CH_2Cl_2, brown crystals were deposited. The X-ray crystallographic studies revealed the *cis*-β configuration (Fig. 4). Both phenoxyimine ligands were found to be deviated from the

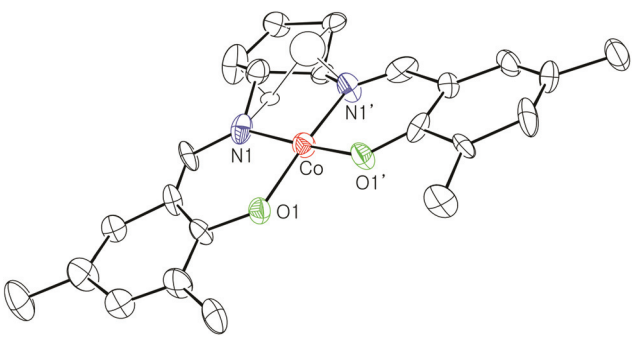


Fig. 2 Thermal ellipsoid plot (30% probability level) of the reduced cobalt(II) complex of **6**.

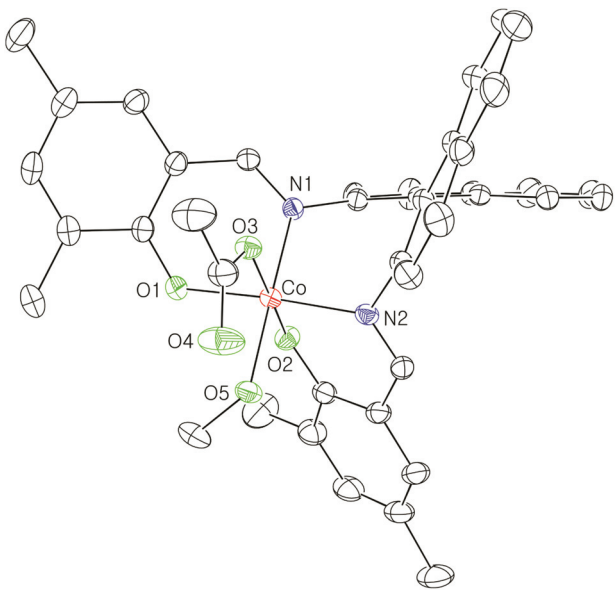


Fig. 3 Thermal ellipsoid plot (30% probability level) of **7** adducted by methanol.

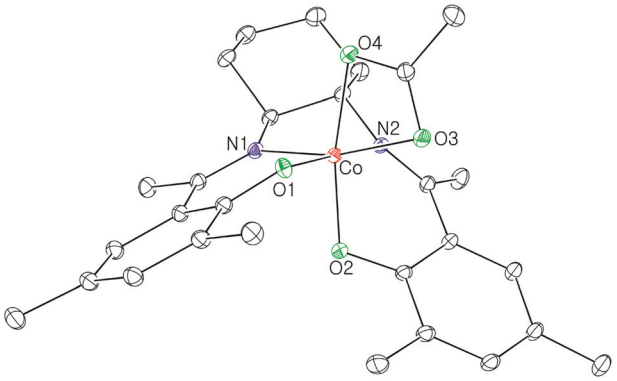
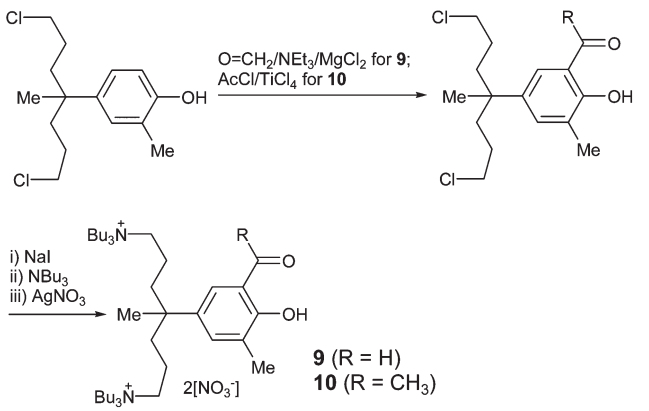


Fig. 4 Thermal ellipsoid plot (30% probability level) of **8**.

formation of a plane with cobalt. The angles between the N═CCC–O plane and the N–Co–O plane were 28.23(5)° and 44.13(5)° for each phenoxyimine cobalt binding. The phenoxyimine situated in a *fac*-arrangement deviated more severely than the phenoxyimine situated in a *mer*-arrangement. In the structure of (Me-salcy)Co(κ^2-OAc), a phenoxyimine situated in a *mer*-arrangement formed a fairly strict plane with cobalt (the angle between the N═CCC–O plane and the N–Co–O plane, 8.8(1)°) whereas the other phenoxyimine situated in a *fac*-arrangement deviated from the stable coplanar structure (the angle between the N═CCC–O plane and the N–Co–O plane, 38.5(1)°). The *trans*-diaminocyclohexane unit was situated in an unstrained chair conformation. The average CCCC torsional angle (59.3°) on the cyclohexane ring was very close to the ideal value of 60°.

Salen–Co(III) complexes tethering quaternary ammonium salts

Inexpensive and large-scale synthesis of salicylaldehyde derivative **9** bearing 2 quaternary ammonium salts was achieved (100 kg per batch).[21,22] A 2′-hydroxyacetophenone derivative bearing 2 quaternary ammonium nitrate salts (**10**) can be prepared by simply replacing the formylation step in the synthetic route of **9** with an acetylation step (eqn (4)). Acetylation was successfully performed using acetyl chloride (1.5 equiv.) and $TiCl_4$ (1.0 equiv.) in a neat condition at 120 °C for 1 h.



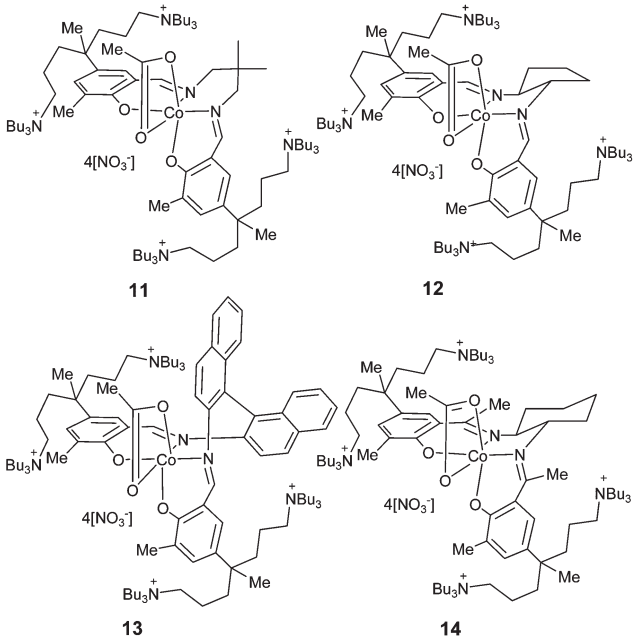
(4)

Condensation reactions of 2,2-dimethyl-1,3-propanediamine, *trans*-1,2-diaminocyclopentane, and 1,1′-binaphthyl-2,2′-diamine with **9** in CH_2Cl_2 result in clean formation of the corresponding Schiff base ligands. From the ligand prepared using 2,2-dimethyl-1,3-propanediamine and *trans*-1,2-diaminocyclopentane, cobalt(III) complexes **11** and **12** were synthesized according to the routine procedure and conditions (metallation using $Co(OAc)_2$ and then oxidation using AgOAc). From the ligand prepared using 1,1′-binaphthyl-2,2′-diamine, metallation using $Co[N(SiMe_3)_2]_2$, but not $Co(OAc)_2$, was successful. Oxidation of the resulting cobalt(II) complex to cobalt(III) acetate **13** was cleanly performed using AgOAc as an oxidant. The imine-bond formation by condensation between **10** and *trans*-1,2-diaminocyclohexane was sluggish under the conditions used for aldimine bond formation, and rather severe conditions were required (refluxing 1-butanol for 2 days). Metallation of the ligand was also not successful when using $Co(OAc)_2$, but it could be successfully achieved by reacting the ligand with $Co[N(SiMe_3)_2]_2$ in CH_3CN. The resulting paramagnetic cobalt(II) complex was cleanly converted to the diamagnetic cobalt(III) complex **14** by oxidation using AgOAc.

The signal patterns of the ^{1}H NMR spectra of **12–14** observed in CD_2Cl_2 were identical to those of model complexes **6–8**. Each half of the ligand framework was magnetically nonequivalent, giving rise to different signals. Two N–C*H* signals were found to be widely separated at 5.15 and 3.55 ppm in the ^{1}H NMR spectrum of **14**. The signal pattern of **11** constructed using flexible 2,2-dimethyl-1,3-propanediamine was similar to those of **12–14**. These observations indicate that **11–14** adopt the *cis*-β configuration in CD_2Cl_2. The signal patterns observed in the ^{1}H NMR spectra in DMSO-d_6 were also similar to those observed for model complexes **6–8**. In the ^{1}H NMR spectra of **11**, **13**, and **14** in DMSO-d_6, a set of characteristic signals assignable to the *cis*-β configuration was observed. The signal pattern of **12** constructed from *trans*-1,2-diaminopentane was the same as that observed for **1** constructed from *trans*-1,2-diaminohexane, even though the signals of **12** were broad. Two sets of signals were observed, a set of symmetric complexes that can be assigned as acetate de-coordinated and another major set of dissymmetric complexes where acetate is coordinated.

Complexes **11**, **13**, and **14** were not active at all in the CO_2/PO copolymerization even at a low [PO]/[Cat] ratio of 10 000. Complex **12** showed activity in CO_2/PO copolymerization under our standard polymerization conditions ([PO]/[Cat] = 100 000, 70 °C, 25 bar CO_2, 1.0 h). The activity (TOF, 12 400 h^{-1}) and selectivity (93%) were both inferior to those attained with **1**. In a previous report, we suggested that the capability to adopt the *cis*-β configuration was related to high activity in CO_2/epoxide copolymerization;[28] however, in this study, cobalt complexes prepared from ligand frameworks that likely adopt the *cis*-β configuration did not show any activity, though these complexes indeed adopted the *cis*-β configuration, even in DMSO-d_6. Thus, the results suggested that the *cis*-β binding mode does not ensure high catalytic activity. In the DMSO-d_6 ^{1}H NMR spectra of active catalysts such as **1**, **12**, and others previously reported, two sets of signals were observed, one of which was assigned to the acetate de-coordinated state. In CO_2/epoxide, a key step may be the nucleophilic attack of the terminal carbonate anion onto a coordinating epoxide. A facile back-side attack easily occurs once the carbonate anion is de-coordinated from the cobalt centre. Thus, it is reasonable to observe the activity for the

complexes that show an acetate de-coordination equilibrium structure in DMSO-d_6. The exceptional high activity observed for **1** remains to be elucidated. As shown in this study and previous reports, variation of the ligand framework results in considerable deterioration of the catalytic performance.[38,39] We proposed that unusual binding underlies the exceptional high activity of **1**, *i.e.*, the coordination of carbonate anions instead of the imine ligand.[16,38]



Experimental section

General procedure and materials

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. CH_2Cl_2, CD_2Cl_2 and $CDCl_3$ were dried by stirring over CaH_2, and they were subsequently vacuum-transferred to reservoirs. DMSO-d_6 was dried over molecular sieves 3 Å. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury Plus 400. Elemental analyses were performed at the Analytical Centre, Kyunghee University. Gel permeation chromatograms (GPC) were obtained at room temperature in $CHCl_3$ using a Waters Millennium apparatus with polystyrene standards. 2-Hydroxy-3,5-dimethylbenzaldehyde,[40] 2-hydroxy-3,5-dimethylacetophenone,[41] *trans*-1,2-diaminocyclopentane,[42] and $Co[N(SiMe_3)_2]_2$ [43] were prepared according to the reported method.

CO_2/EO copolymerization

A 3 L bomb reactor equipped with a mechanical stirrer was charged with EO (790 g). A solution of catalyst **1** (0.075 g, 0.045 mmol, [EO]/[cat] = 400 000) in EO (10 g) was charged in the reactor. The CO_2 gas was pressurized up to 12 bar, and then the temperature was increased to 70 °C. The pressure was increased with increasing temperature to reach a steady pressure of 30 bar. After 1.5 h from the initial heating, the pressure started to decrease. After polymerization was initiated, CO_2 gas was continuously fed with a mass flow controller (MFC) at 30 bar to compensate for the consumed CO_2. The polymerization was performed for 2 h, and the resulting thick-viscous polymer solution was then transferred to a 5 L reservoir equipped with a mechanical stirrer. The polymer solution was diluted with methylene chloride (3 L). After the CO_2 pressure was released, the polymer solution in methylene chloride was filtered through a silica pad (70 g) that had been wetted with methylene chloride. After removal of the methylene chloride, the residue was dried in a vacuum oven at 60 °C overnight. The isolated polymer weighed 146 g (entry 4 in Table 1).

Preparation of 3. 2-Hydroxy-3,5-dimethylbenzaldehyde (500 mg, 3.33 mmol) was weighed into a round bottom flask in a glove box, and then (±)-*trans*-1,2-diaminocyclopentane (167 mg, 1.66 mmol) and methylene chloride (7 mL) were added. The reaction mixture was stirred overnight at room temperature. The solution was filtered through Celite, and the solvent was removed under reduced pressure. A yellow solid was obtained in a quantitative yield that was sufficiently pure for use in the next reaction without further purification (580 mg, 96%). IR (KBr): 3209 (OH), 1627 (C═N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 13.32 (s, 2H, OH), 8.21 (s, 2H, N═CH), 6.99 (s, 2H, *m*-H), 6.83 (s, 2H, *m*-H), 3.72 (s, 2H, N–CH), 2.25 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 1.96 (br, 6H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.68, 156.85, 134.28, 129.07, 127.19, 125.44, 117.58, 65.95, 33.36, 22.26, 20.55, 15.67 ppm. Anal. calc. ($C_{23}H_{28}N_2O_2$): C, 75.79; H, 7.74; N, 7.69%. Found: C, 75.47; H, 7.39; N, 7.95%.

Preparation of 4. 2-Hydroxy-3,5-dimethylbenzaldehyde (500 mg, 3.33 mmol) and 1,1′-binaphthyl-2,2′-diamine (473 mg, 1.66 mmol) were dissolved in ethanol–acetic acid (7 : 1 v/v, 10 mL) and stirred overnight at 60 °C. After removal of the solvent under vacuum, the residue was subsequently triturated in hexane (2 mL). A yellow solid was obtained in 97% yield (885 mg). IR (KBr): 3565 (OH), 1623 (C═N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.97 (s, 2H, OH), 8.51 (s, 2H, N═CH), 8.04 (d, J = 8.4 Hz, 2H, CH), 7.93 (d, J = 8.4 Hz, 2H, CH), 7.53 (d, J = 8.4 Hz, 2H, CH), 7.43 (t, J = 8.0 Hz, 2H, CH), 7.25 (m, 4H, CH), 6.90 (s, 2H, *m*-H), 6.77 (s, 2H, *m*-H), 2.17 (s, 6H, CH_3), 2.04 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.97, 156.95, 144.70, 135.00, 133.27, 132.34, 129.90, 129.86, 128.40, 128.22, 127.01, 126.83, 126.51, 125.70, 125.57, 118.21, 117.91, 20.47, 15.67 ppm. Anal. calc. ($C_{38}H_{32}N_2O_2$): C, 83.18; H, 5.88; N, 5.11%. Found: C, 82.84; H, 5.65; N, 5.40%.

Preparation of 5. 2-Hydroxy-3,5-dimethylacetophenone (1.04 g, 6.33 mmol) and (±)-*trans*-1,2-diaminocyclohexane (361 mg, 3.17 mmol) were weighed into a round bottom flask, and then 1-butanol (10 mL) was added. The solution was refluxed for 2 days under a N_2 atmosphere. After the solution was cooled to room temperature, the solvent was removed under reduced pressure. The resulting yellow powder was subsequently triturated in hexane (5 mL). The yield was 97% (1.25 g). IR (KBr): 3502 (OH), 1615 (C═N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 16.55 (s, 2H, OH), 7.04 (s, 2H, *m*-H), 6.97 (s, 2H, *m*-H), 3.88 (m, 2H, N–CH), 2.26 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 1.94 (br, 4H, CH_2), 1.97 (br, 2H, CH_2), 1.89 (m, 2H,

CH_2), 1.73 (m, 2H, CH_2), 1.48 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.76, 159.92, 134.17, 126.67, 125.92, 124.99, 117.88, 63.00, 32.78, 24.51, 20.87, 16.16, 14.74 ppm. Anal. calc. ($C_{26}H_{34}N_2O_2$): C, 76.81; H, 8.43; N, 6.89%. Found: C, 76.44; H, 8.32; N, 7.24%.

Preparation of complex 6. To a flask containing **3** (200 mg, 0.548 mmol) and $Co(OAc)_2$ (97.0 mg, 0.548 mmol), methylene chloride (3 mL) was added under a N_2 atmosphere. The solution was stirred at room temperature for 12 h to give a reddish solution, to which AgOAc (91.6 mg, 0.548 mmol) was added. The color of the solution changed to dark brown upon addition of AgOAc. After the solution was stirred for 12 h, it was filtered through Celite. The solvent was removed under reduced pressure to give a dark-brown solid (250 mg, 95%). ^1H NMR (DMSO-d_6) data for the major set: δ 7.57 (s, 1H, N═CH), 7.53 (s, 1H, CH═N), 7.10–6.92 (br s, 4H, *m*-H), 4.49 (br, 1H, N–CH), 4.25 (br, 1H, N–CH), 2.55 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.39 (br, 2H, CH_2), 2.35 (br, 2H, CH_2), 2.19 (s, 6H, CH_3), 1.74 (br, 2H, CH_2), 1.66 (s, 3H, acetate-CH_3) ppm. Data for the minor set: δ 7.72 (s, 2H, N═CH), 7.17 (s, 2H, *m*-H), 7.13 (s, 2H, *m*-H), 4.28 (br, 2H, NCH), 2.60 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 2.40–1.70 (br, 6H, CH_2), 1.66 (s, 3H, acetate-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.00, 157.19, 139.20, 134.36, 132.36, 131.68, 129.26, 127.39, 125.56, 117.92, 76.85, 33.39, 20.46, 20.25, 17.10, 15.64 ppm. Anal. calc. ($C_{25}H_{29}CoN_2O_4$): C, 62.50; H, 6.08; N, 5.83%. Found: C, 62.14; H, 5.96; N, 5.64%.

Preparation of complex 7. Compound **4** (200 mg, 0.364 mmol) and $Co[N(SiMe_3)_2]_2$ (138 mg, 0.364 mmol) were dissolved in acetonitrile (4 mL), and the solution was then stirred overnight at room temperature to obtain a reddish solution. After the solvent was removed under vacuum, the residue was triturated in diethyl ether. To a flask containing the obtained red powder, AgOAc (60.8 mg, 0.364 mmol) was added with methylene chloride (3 mL). The solution changed to a dark-brown colour, and it was then stirred for an additional 12 h. The solution was filtered through Celite, and the solvent was removed under reduced pressure to obtain the desired complex (228 mg, 94%). ^1H NMR (DMSO-d_6): δ 8.11 (d, J = 8.8 Hz, 2H, CH), 7.91 (d, J = 8.0 Hz, 1H, CH), 7.86 (d, J = 8.8 Hz, 1H, CH), 7.79 (s, 1H, N═CH), 7.69 (d, J = 8.0 Hz, 1H, CH), 7.58 (t, J = 7.6 Hz, 1H, CH), 7.49 (t, J = 7.6 Hz, 1H, CH), 7.39 (t, J = 7.6 Hz, 1H, CH), 7.29 (t, J = 7.6 Hz, 1H, CH), 7.22 (s, 1H, N═CH), 7.15 (d, J = 8.0 Hz, 1H, CH), 7.00 (d, J = 11.6 Hz, 1H, CH), 6.97 (d, J = 11.6 Hz, 1H, CH), 6.96 (s, 1H, *m*-H), 6.92 (s, 1H, *m*-H), 6.78 (s, 1H, *m*-H), 6.77 (s, 1H, *m*-H), 2.22 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.61 (s, 3H, acetate-CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 192.76, 169.13, 167.91, 165.95, 163.66, 147.92, 146.65, 137.80, 137.24, 133.03, 132.97, 132.88, 132.69, 132.61, 131.66, 130.92, 130.20, 129.97, 129.43, 128.78, 128.65, 128.00, 127.38, 127.28, 127.08, 126.87, 126.59, 126.38, 126.25, 126.08, 124.15, 124.09, 123.49, 121.97, 119.75, 23.48, 20.29, 20.04, 17.80, 17.68 ppm. Anal. calc. ($C_{40}H_{33}CoN_2O_4$): C, 72.28; H, 5.00; N, 4.21%. Found: C, 71.90; H, 4.78; N, 4.60%.

Preparation of complex 8. This compound was prepared by the same procedure and conditions as that of complex **7** using compound **5**. ^1H NMR (DMSO-d_6): δ 7.23 (s, 1H, *m*-H), 7.02 (s, 1H, *m*-H), 6.93 (s, 1H, *m*-H), 6.59 (s, 1H, *m*-H), 3.77 (br, 1H, N–CH), 3.03 (br, 1H, N–CH), 2.78 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 2.36 (br, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.69 (s, 3H, acetate-CH_3), 1.57 (s, 3H, CH_3), 1.38 (br, 2H, CH_2), 1.26 (br, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 190.57, 176.84, 170.47, 164.53, 162.01, 134.97, 134.10, 133.58, 132.38, 131.65, 126.67, 126.16, 124.24, 122.07, 74.25, 72.41, 34.19, 33.66, 26.77, 25.18, 23.49, 21.05, 20.90, 20.03, 19.85, 17.80, 16.61 ppm. Anal. calc. ($C_{28}H_{35}CoN_2O_4$): C, 64.36; H, 6.75; N, 5.36%. Found: C, 63.99; H, 6.39; N, 5.57%.

Preparation of 10. $TiCl_4$ (1.81 g, 9.55 mmol) was slowly added to 2-Me-4-[$\{Cl(CH_2)_3\}_2$CMe]-C_6H_3OH (2.51 g, 8.68 mmol) placed in a flask under a N_2 atmosphere at room temperature. The resulting dark red solution was stirred until gas evolution ceased. CH_3COCl (1.02 g, 13.0 mmol) was added to the resulting solid. After the resulting thick solution was stirred at room temperature for 15 min, it was warmed to 120 °C and stirred for an additional 1 h. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (30 mL), and quenched with H_2O (30 mL). The organic phase was collected and washed with H_2O (20 mL) twice. After CH_2Cl_2 was dried over anhydrous $MgSO_4$, the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography on a silica gel eluting with hexane and diethyl ether (v/v, 20 : 1). The yield was 65% (1.85 g). From the isolated 2-Me-4-[$\{Cl(CH_2)_3\}_2$-CMe]-6-(CH_3CO)–C_6H_2OH, the desired compound **10** was prepared according to the same procedure and conditions employed for the synthesis of salicylaldehyde derivative **9** *via* 3 steps: exchange of chloride with iodide using NaI, nucleophilic attack of tributylamine, and I^- exchange with NO_3^- using $AgNO_3$.[21] IR (KBr): 3447 (OH), 1633 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 12.57 (s, 1H, OH), 7.63 (s, 1H, *m*-H), 7.38 (s, 1H, *m*-H), 3.39–3.10 (br, 16H, NCH_2), 2.73 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 1.83–1.45 (br, 18H, CH_2), (r, 14H, CH_2), 1.36 (s, 3H, CH_3), 1.35 (br, 14H, CH_2), 0.90 (t, J = 7.2 Hz, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 205.78, 158.99, 136.66, 135.08, 127.15, 125.99, 118.19, 60.36, 59.15, 53.61, 40.26, 36.30, 28.82, 26.83, 24.30, 19.90, 18.75, 15.98, 13.89 ppm. Anal. calc. ($C_{41}H_{78}N_4O_8$): C, 65.22; H, 10.41; N, 7.42%. Found: C, 64.88; H, 10.10; N, 7.20%.

Preparation of complex 11. Compound **9** (400 mg, 0.540 mmol) was weighed into a round-bottom flask in a glove box, and then, 2,2-dimethyl-1,3-propanediamine (27.6 mg, 0.270 mmol) and methylene chloride (5 mL) were added. The reaction mixture was stirred overnight at room temperature. The solution was filtered through Celite and the solvent was removed under reduced pressure. The yield for the formation of the ligand was 98% (408 mg), and the obtained yellow solid was sufficiently pure for use without further purification. To the flask containing the ligand, $Co(OAc)_2$ (47.8 mg, 0.270 mmol) and methylene chloride (5 mL) were added. The solution was stirred at room temperature for 12 h to give a reddish solution, to which AgOAc (45 mg, 0.27 mmol) was added. The color of the solution immediately changed to dark brown. After the solution was stirred for 12 h, it was filtered through Celite. The solvent was removed under reduced pressure to obtain a dark-brown solid in

a quantitative yield. ^{1}H NMR (DMSO-d_6): δ 7.88 (br s, 1H, *m*-H), 7.46 (br s, 1H, *m*-H), 7.15 (br s, 1H, *m*-H), 7.07 (s, 2H, N═CH), 6.88 (br s, 1H, *m*-H), 4.34 (br, 2H, N–CH_2), 3.57 (br, 2H, N–CH_2), 3.25–2.92 (br, 32H, NCH_2), 1.63 (s, 6H, CH_3), 1.60–1.36 (br, 32H, CH_2), 1.36–1.13(br m, 35H), 1.06 (s, 6H, CH_3), 0.98–0.77(br m, 36H, CH_3) ppm.

Preparation of complex 12. The ligand of this compound was prepared by the same procedure as that of **11** using *trans*-1,2-diaminocyclopentane. A yellow solid was obtained in a quantitative yield and was sufficiently pure enough for use without further purification. The metallation and oxidation processes were the same as those of **11**. ^{1}H NMR (DMSO-d_6) data for the major set: δ 7.65 (s, 1H, N═CH), 7.63 (s, 1H, CH═N), 7.30–7.16 (br s, 4H, *m*-H), 4.51 (br, H, N–CH), 4.26 (br, H, N–CH), 3.33–2.92 (br, 32H, NCH_2), 2.65–2.32 (br, 6H, CH_3), 2.08–1.82 (br, 4H, cyclopentyl-CH_2), 1.70–1.12 (br m, 75H), 1.05–0.77 (br, 36H, CH_3) ppm. Data for the minor set: δ 7.82 (s, 2H, N═CH), 7.39 (s, 2H, *m*-H), 7.33 (s, 2H, *m*-H), 4.26 (br, 2H, N–CH), 3.33–2.92 (br, 32H, NCH_2), 2.65–2.32 (br, 6H, CH_3), 2.08–1.82 (br, 4H, cyclopentyl-CH_2), 1.70–1.12 (br m, 75H), 1.05–0.77 (br, 36H, CH_3) ppm.

Preparation of complex 13. The ligand of this compound was prepared by the same procedure as that of **4**, using **9** instead of 2-hydroxy-3,5-dimethylbenzaldehyde. A yellow solid was obtained in a quantitative yield and was sufficiently pure for use without further purification. The metallation and oxidation processes were same as those of **7**. ^{1}H NMR (DMSO-d_6): δ 8.13 (d, J = 8.8 Hz, 1H, CH), 8.12 (d, J = 8.0 Hz, 1H, CH), 7.95 (d, J = 8.4 Hz, 1H, CH), 7.89 (d, J = 8.8 Hz, 1H, CH), 7.88 (s, 1H, *m*-H), 7.62 (d, J = 8.4 Hz, 1H, CH), 7.60 (t, J = 7.6 Hz, 1H, CH), 7.52 (t, J = 7.6 Hz, 1H, CH), 7.40 (t, J = 7.6 Hz, 1H, CH), 7.34 (s, 1H, *m*-H), 7.32 (t, J = 8.0 Hz, 1H, CH), 7.16 (s, 1H, N═CH), 7.11 (s, 1H, N═CH), 7.11 (d, J = 6.8 Hz, 1H, CH), 6.97 (s, 2H, *m*-H), 6.96 (d, J = 8.4 Hz, 1H, CH), 6.92 (d, J = 8.8 Hz, 1H, CH), 3.26–2.90 (br, 32H, NCH_2), 2.25 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.57–1.33 (br, 32H, CH_2), 1.33–1.09 (br m, 35H), 1.70–1.05 (br m, 73H), 1.00–0.76 (br m, 36H, CH_3) ppm.

Preparation of complex 14. The ligand of this compound was prepared by the same procedure as that of **5** using **10** instead of 3,5-dimethyl-2-hydroxybenzaldehyde. A yellow solid was obtained in a quantitative yield and was sufficiently pure for use without further purification. The metallation and oxidation processes were the same as those of complex **8**. ^{1}H NMR (DMSO-d_6): δ 7.27 (s, 1H, *m*-H), 7.11 (s, 1H, *m*-H), 7.08 (s, 1H, *m*-H), 6.77 (s, 1H, *m*-H), 4.94 (br, 1H, N–CH), 3.76 (br, 1H, N–CH), 3.34–2.92 (br, 32H, NCH_2), 2.83 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.96 (br, 2H, cyclohexyl-CH_2) 1.80–1.12 (br m, 82H), 1.00–0.76(br m, 36H, CH_3) ppm.

X-ray structural determination

The crystallographic measurements were performed at 100 K using a Bruker APEX II CCD-based diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The reflection data were collected as multi-scan frames with 0.5° per frame and an exposure time of 10 s per frame. Cell parameters were determined and refined by the SMART program. Data reduction was performed using SAINT software. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were calculated at idealized positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Crystallographic data for the reduced cobalt(II) complex of **6** (CCDC 894116): $C_{23}H_{26}CoN_2O_2$, M = 421.39, monoclinic, a = 24.891(5), b = 11.215(2), c = 7.3326(15) Å, β = 104.80(3)°, V = 1979.1(7) Å^3, T = 293 (2) K, space group $C2/c$, Z = 4, 4416 reflections measured, 1740 unique ($R_{(int)}$ = 0.0680) which were used in all calculations. The final wR_2 was 0.1088 ($I > 2\sigma(I)$). Crystallographic data for **7**·CH_3OH·(CH_2Cl_2) (CCDC 894115): $C_{42}H_{39}Cl_2CoN_2O_5$, M = 781.58, triclinic, a = 9.8572(2), b = 12.4423(9), c = 17.1598(12) Å, α = 111.160(2), β = 102.001(3), γ = 91.009(3)°, V = 1909.9(2) Å^3, T = 100 (2) K, space group $P\bar{1}$, Z = 2, 27 710 reflections measured, 6689 unique ($R_{(int)}$ = 0.0156) which were used in all calculations. The final wR_2 was 0.0915 ($I > 2\sigma(I)$). Crystallographic data for **8**·(CH_2Cl_2) (CCDC 894114): $C_{29}H_{37}Cl_2CoN_2O_4$, M = 607.44, triclinic, a = 10.0530(3), b = 11.5924(3), c = 12.9469(4) Å, α = 111.8210(10), β = 94.2400(10), γ = 101.0300(10)°, V = 1357.30(7) Å^3, T = 100 (2) K, space group $P\bar{1}$, Z = 2, 16 948 reflections measured, 5000 unique ($R_{(int)}$ = 0.0230) which were used in all calculations. The final wR_2 was 0.0779 ($I > 2\sigma(I)$).

Conclusions

Cobalt(III) complex (**1**) of the salcy-type ligand tethering 4 quaternary ammonium salts is as highly active in CO_2/EO copolymerization as it is in CO_2/PO copolymerization. A TOF of up to 25 900 h^{-1} (TON, 518 000; 2.72 kg polymer per g cat) was achieved with the formation of a negligible amount of ethylene carbonate. High-molecular-weight polymers (M_n, 200 000–300 000) with strictly alternating repeating units were generated. We attempted to prepare effective catalysts based on **1** by altering the ligand structure, especially aiming at cobalt complexes favourable for formation of the *cis*-β configuration. Complexes **11**, **13**, and **14** consistently adopted a single binding mode of the *cis*-β configuration. The binding mode of the *cis*-β configuration was unambiguously confirmed by X-ray crystallography studies and NMR studies of model complexes not bearing quaternary ammonium salt units. Complexes that take on the *cis*-β configuration do not show any activity in CO_2/PO copolymerization, whereas complex **12**, which fluctuates in DMSO between coordination and de-coordination of the acetate ligand, shows fairly high activity (TOF, 12 400 h^{-1}). This fluxional behaviour may be critical for the catalyst cycle because a facile back-side attack easily occurs from the de-coordinated carbonate anion. However, complex **12** still does not compete with **1** in terms of activity, selectivity, and the catalyst cost.

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