

Salicy-Naphthalene Cobalt Complexes as Catalysts for the Synthesis of High Molecular Weight Polycarbonates

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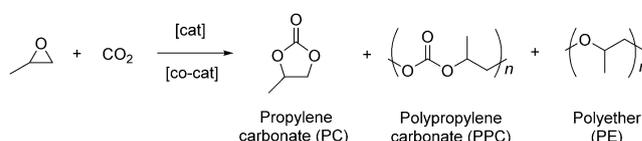
High molecular weight polypropylene carbonates were prepared by CO₂/propylene oxide copolymerization catalyzed by salicy-naphthalene cobalt complexes. The introduction of methyl groups in the *ortho* position of naphthalene-based

salicy ligands and the catalyst loading in the presence of hexane as a co-solvent were crucial to enhance the catalytic performance for the production of polycarbonates of high molecular weight.

Introduction

In recent years, the utilization of CO₂ in the synthesis of value-added products has been the focus of both academic and industrial communities.^[1] The reaction of carbon dioxide with epoxides has been widely studied as a route to obtain cyclic carbonates and polycarbonates (Scheme 1). In this process, cyclic carbonates are usually the main products as they are thermodynamically favored.^[2] Other by-products such as polyethers can also be obtained.

A number of patents and papers have appeared during the last decades for the production of polycarbonates through coupling of epoxides with CO₂ in the presence of homogeneous catalytic systems such as Co^{III}-salen based catalysts.^[3] Polycarbonates are valuable products for industry as they are both environmentally friendly and cheap with a wide range of interesting applications. In particular, high molecular weight polypropylene carbonate (PPC, Scheme 1) is a biodegradable polymer used in packaging, agricultural and biomedical industries. Furthermore, the application of PPC for producing scaffolds for tissue engineering applications has also been described.^[4] For these applications high molecular weight polycarbonates are usually desired.



Scheme 1. Catalytic reaction between propylene oxide and CO₂ promoted by an organometallic catalyst and co-catalyst.

A large effort has been devoted to the production of this polymer since PPC was first synthesized by Inoue et al. in 1969.^[5] A crucial point in the development of the direct copolymerization of CO₂ and propylene oxide was the design of new catalytic systems that were cheap, highly productive and selective to polypropylene carbonate. In the early 2000s, systematic studies on a bimetallic zinc catalytic system containing β -diiminate ligands were reported by Coates and co-workers.^[6] In these reports, the presence of *ortho* substituents at the *N*-aryl moieties were revealed as crucial for the catalyst activity and selectivity to polypropylene carbonate. Cobalt-salen-OAc catalysts were also described for the copolymerization of PO/CO₂, producing PPC with 99% carbonate linkages.^[3c] In 2004, Lu and co-workers reported for the first time a binary system containing a Co^{III}-salicy complex and a nucleophilic co-catalyst, that improved the performance and the stability of the catalytic species.^[7]

A few years later, important studies were performed simultaneously by the groups of Coates^[8] and Lu,^[9] in which the axial ligands of the salicy-complexes, the nature of the co-catalysts, temperature, CO₂ pressure and catalyst loadings were optimized. Producing high molecular weight copolymers (for instance $M_w = 80\,000\text{--}300\,000$) using the binary systems previously mentioned was one of the main drawbacks.

A second generation of functionalized Co^{III}-salicy catalysts bearing cationic substituents in the aryl group was described and developed by various authors and they remain the most active catalysts for the CO₂/propylene oxide copolymerization reported to date (Figure 1).^[10–12] Owing to the high stability of

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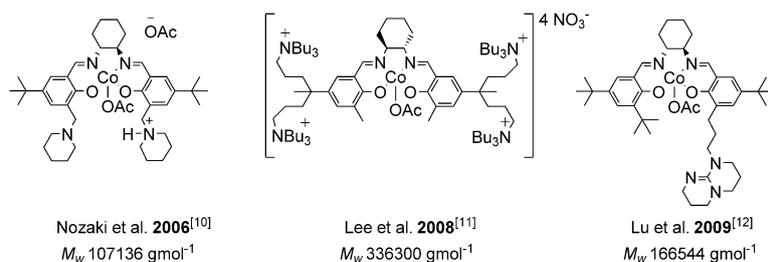


Figure 1. Catalysts with the highest activity reported for the copolymerization CO_2/PO .

these systems, particularly to its living nature, the molecular weights of the copolymers obtained were higher than those obtained for the polycarbonates previously reported in the literature. However, despite the excellent performance of these systems, these types of ligands require multi-step syntheses with moderate to low overall yield.

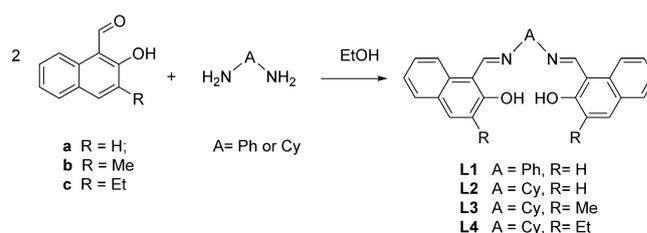
In comparison with phenyl, naphthyl moieties have an extended π -conjugation^[13a] that can influence the stability of the metal complex favorably and we expect also in the catalytic activity. Here, we report the synthesis of new naphthalene-based ligands **L1–L4** containing -H or an alkyl substituent in *ortho*-position and their corresponding cobalt (III) complexes (Figure 2). These complexes were tested in the CO_2/PO copolymerization reaction and exhibited high activity in this process for the production of high-molecular weight copolymers.

Results and Discussion

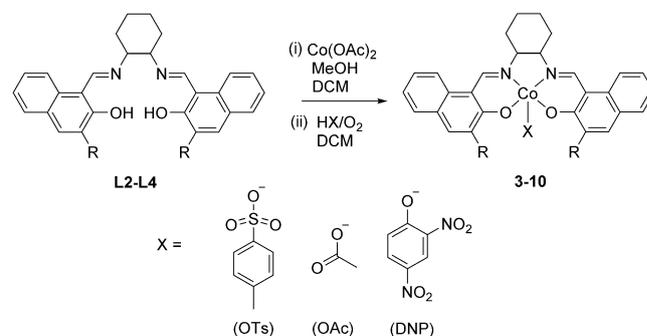
Preparation and characterization of salicy-naphthalene ligands and complexes

The ligands **L1–L4** were obtained by condensation from the corresponding salicylaldehyde fragments **a–c** (Scheme 2). The fragments **b–c** were obtained by *ortho*-formylation procedure starting from the corresponding naphthols.^[13b,c]

The $\text{Co}(\text{L})\text{X}$ complexes were prepared by reaction of these ligands with cobalt(II) acetate followed by oxidation of the metal center in the presence of an acid (Scheme 3). The complexes **1**, **2**, **3** and **6** were previously reported using similar pro-



Scheme 2. General scheme for the synthesis of naphthalene based salen ligands **L1–L4**.



Scheme 3. General scheme for the synthesis of $\text{Co}(\text{salicy})\text{X}$ complexes.

cedures.^[13–15] All the complexes were obtained in high yields and isolated as brown or green solids.

These Co complexes were characterized by NMR, IR and mass spectroscopy electrospray ionization-time-of-flight (ESI-TOF) techniques (See the Experimental Section).

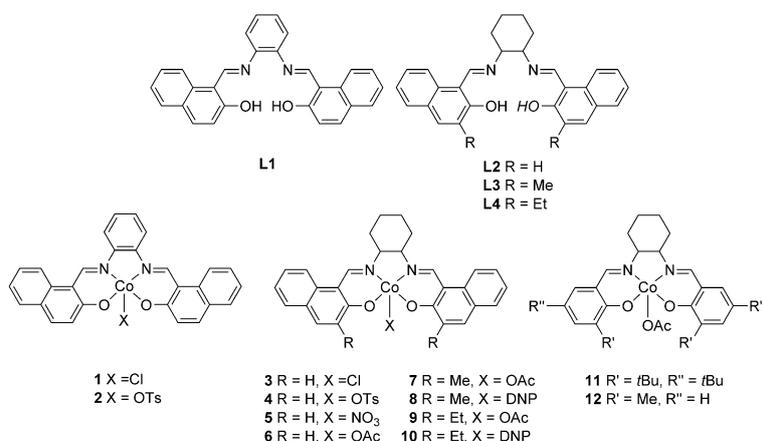


Figure 2. Ligands and corresponding Co-complexes used in this study.

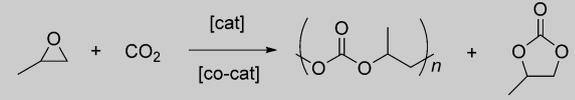
Carbon dioxide/ propylene oxide copolymerization reactions: Study of the reaction parameters and catalyst variations.

The synthesized cobalt complexes 1–6 (Figure 2) were first tested in the copolymerization of carbon dioxide and propylene oxide at room temperature and in the presence of tetrabutyl ammonium bromide (TBAB) as co-catalyst. The results are listed in Table 1. Under these conditions, the salphen complexes 1 and 2 (Table 1) afforded the corresponding cyclic carbonate in high (entry 2) and low yield (entry 1). In the case of salicy complexes, moderate yields were observed whereas the selectivity revealed to be dependent on the X group coordinated to the Co center. If X = Cl (3) or NO₃ (5) (entries 3 and 5), the main product was the cyclic carbonate whereas for X = tosylate (4) or acetate (6) the selectivity was switched in favor of the polypropylene carbonate (entries 4, 6–8).

On increasing the temperature to 40 °C, an increase of the productivity to PPC was observed without any loss of selectivity (entry 6). This temperature was therefore used for the following experiments. It had been previously suggested that the use of bromide or iodide favors the backbiting after the first carbon dioxide/PO insertions and thus the selectivity towards the cyclic carbonates. Similar cocatalysts effect has previously been observed.^[2b,9] Bis(triphenylphosphine)iminium chloride (PPNCl) was thus used as co-catalyst to improve the selectivity to PPC although in our case, only a slight increase in selectivity was detected (entry 7).

The new Co complex 7 containing methyl groups in *ortho* position of the naphthalene ring (Figure 2) was tested under the previously optimized conditions (Table 2). The values for productivity and selectivity were similar to those obtained for the original complex 6 (entries 1 and 2). However, an increase in the molecular weight of the product was detected, suggesting a higher stability of the catalytic species. To optimize the productivity (TON) of the catalyst, the Co loading was varied

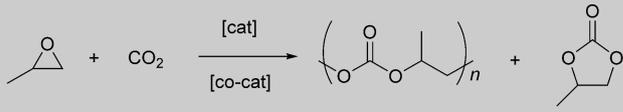
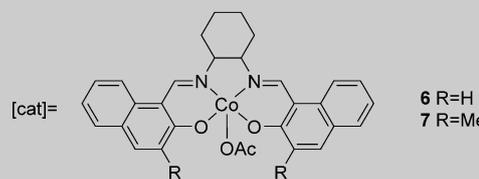
Table 1. Effect of the axial ligand and the temperature in CO₂/propylene oxide coupling reaction using catalysts 1–6.^[a]



Entry	Catalyst	Yield [%]	TON ^[b]	PPC:PC:PE ^[c]
1 ^[d]	1	12	115	0:99:1
2 ^[d]	2	96	955	0:99:1
3	3	53	533	0:99:1
4	4	29	289	90:8:3
5	5	5	50	0:99:1
6 ^[e]	4	60	603	92:5:3
7 ^[e,f]	4	66	660	94:1:5
8 ^[e,f]	6	53	531	87:12:0

[a] Co-catalyst TBAB; [PO]:[TBAB]:[Co] = 1000:1:1; 2 mL PO (28.6 mmol), 25 °C, 30 bar, 16 h. [b] Calculated as (mol product)/(mol catalyst). [c] PPC = polypropylene carbonate, PC: propylene carbonate, PE: polyether in the crude mixture. [d] 72 hours; [e] 40 °C. [f] Using bis(triphenylphosphine)iminium chloride as co-catalyst.

Table 2. Effect of the catalyst loading (7) for the CO₂/propylene oxide reaction.^[a]

Entry	Cat.	Mol%	Yield [%]	Select. ^[b] [%]	TON ^[c]	M _w [g mol ⁻¹]	PDI
1	6	0.1	53	87	531	17 500	1.20
2	7	0.1	51	84	510	31 100	1.47
3	7	0.05	69	97	1380	48 300	1.25
4	7	0.02	63	95	3150	104 000	1.43
5	7	0.01	40	93	4310	92 800	1.34
6	7	0.005	21	96	4279	70 000	1.17

[a] [PPNCl]:[Co] = 1:1; 2 mL PO (28.6 mmol), 40 °C, 30 bar, 16 h. Carbonate linkages of the resulted polycarbonates are >99% based on ¹H NMR spectroscopy. [b] Selectivity for the polycarbonate over the cyclic carbonate in unit of % determined by ¹H NMR spectroscopy of the crude product. [c] Calculated as (mol product)/(mol catalyst).

between 0.1 and 0.005 mol% using complex 7 (Table 2, entries 2–6 and Figure 3). By decreasing the loading down to 0.02 mol%, both productivities and molecular weights were found to increase (entry 4). However, if the loading was further lowered, the productivities still increased whereas the molecular weights decreased. The moderate molecular weight obtained at 0.005 mol% (entry 6) suggested that the catalyst/co-catalyst system was not acting as a tandem under these conditions. It was concluded from these experiments that the best compromise between productivity and molecular weight was obtained at 0.01 mol% Co loading (entry 5 and Figure 3). However, if catalyst 6 was tried under increased dilutions (0.01 mol%) no catalytic activity was observed.

Next, a series of new salicy Co complexes containing alkyl substituents and with different axial ligands (X) were evaluated for the CO₂/propylene oxide copolymerization reaction. The results are summarized in Table 3.

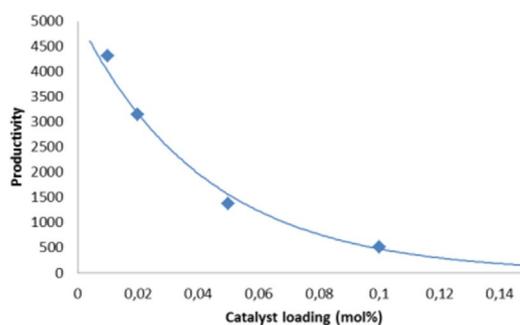
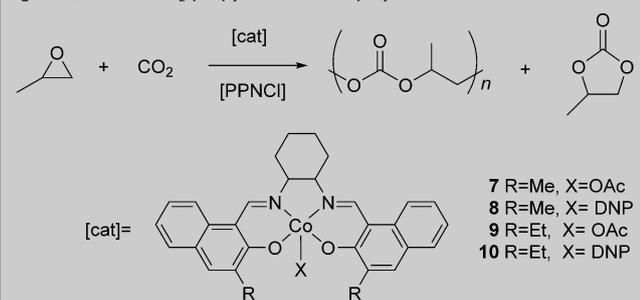


Figure 3. Catalyst loading vs. productivity (TON) of the reaction catalyzed by 7/PPNCl.

Table 3. Effect of the *ortho*-alkyl substituent and nature of the axial ligand (X) in the CO₂/propylene oxide copolymerization.^[a]


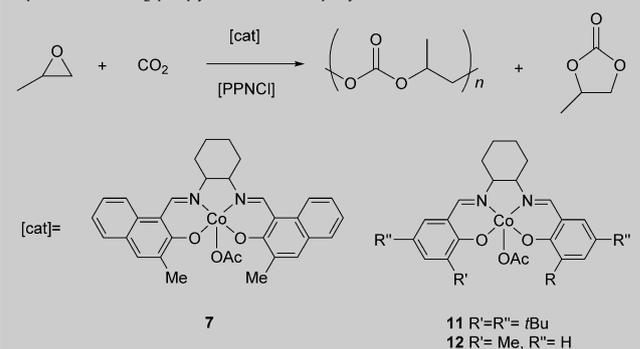
Entry	Cat.	Yield [%]	TON ^[b]	Select. ^[c] [%]	M _n [g mol ⁻¹]	M _w [g mol ⁻¹]	PDI
1	7	63	3150	95	72 700	104 000	1.43
2	8	72	3600	96	84 900	106 100	1.25
3	9	51	2451	85	38 600	46 300	1.20
4	10	8	793	17	n.d.	n.d.	n.d.

[a] 0.02 mol% cat, 30 bar, 16 h, 40 °C. Carbonate linkages of the resulted polycarbonates are > 99% based on ¹H NMR spectroscopy. [b] Calculated as (mol Product)/(mol Catalyst). [c] Selectivity for the polycarbonate over the cyclic carbonate in unit of % determined by ¹H NMR spectroscopy of the crude product.

If the catalyst bearing a 2,4-dinitrophenolate counter-anion and a methyl substituted ligand (catalyst **8**, entry 2) was used, similar results to those obtained with catalyst **7** (X = OAc) were achieved: the copolymerization was efficient (72% yield) and the product exhibited high molecular weight (106 000 g mol⁻¹). If catalysts bearing the ligand **L4** (complexes **9** and **10**) that contains ethyl groups in *ortho*-position of the naphthyl moieties were used (entries 3–4), the productivity, the selectivity and the molecular weight were lower than using the analogue systems **7** and **8**. These results indicated the high sensitivity of these systems to the steric hindrance induced by the presence of *ortho*-substituents. Regarding the stereoselectivity of the materials obtained with the new complexes, in all cases the PPC with > 79% HT connectivity was achieved. To compare our system with the best binary systems reported for this reaction, the complex **11** bearing *tert*-butyl groups in *ortho*-position of the model salicy ligand and previously described in the literature by Coates and co-workers,^[3c] was tested at Co loading of 0.005 mol% (Table 4, entry 3). In this case, the yield and molecular weight were slightly lower than those obtained for complex **7**. If the Me-substituted complex **12** was tested in the copolymerization reaction (Table 4, entry 4), higher productivity, and molecular weight values were obtained.

To improve the performance of our system we decided to add hexane as a co-solvent to control the concentration of the catalyst working at the same diluted conditions (Table 4, entry 2). Under these conditions, the molecular weight improved at lower conversions increasing the efficiency of the total process.

Based on the mechanism previously proposed in this reaction (Scheme 4),^[3b] the increase in molecular weight observed in this study could be explained by the destabilization

Table 4. Comparison results with other salicy-cobalt complexes previously reported for CO₂/propylene oxide copolymerization reaction.^[a]


Entry	Cat.	Yield [%]	TON ^[b]	Select. ^[c] [%]	M _n [g mol ⁻¹]	M _w [g mol ⁻¹]	PDI
1	7	21	4279	96	56 900	70 000	1.23
2 ^[d]	7	16	1649	99	63 803	13 5900	2.13
3	11	17	3380	96	48 200	60 700	1.26
4	12	35	7038	99	103 600	128 400	1.24

[a] 0.005 mol% cat and PPNCI, 40 °C, 30 bar, 16 hours. Carbonate linkages of the resulted polycarbonates are > 99% based on ¹H NMR spectroscopy [b] Calculated as (mol Product)/(mol Catalyst). [c] Selectivity for the polycarbonate over the cyclic carbonate in unit of % determined by ¹H NMR spectroscopy of the crude product. [d] Using hexane as a co-solvent in 1:1 ratio PO/hexane.

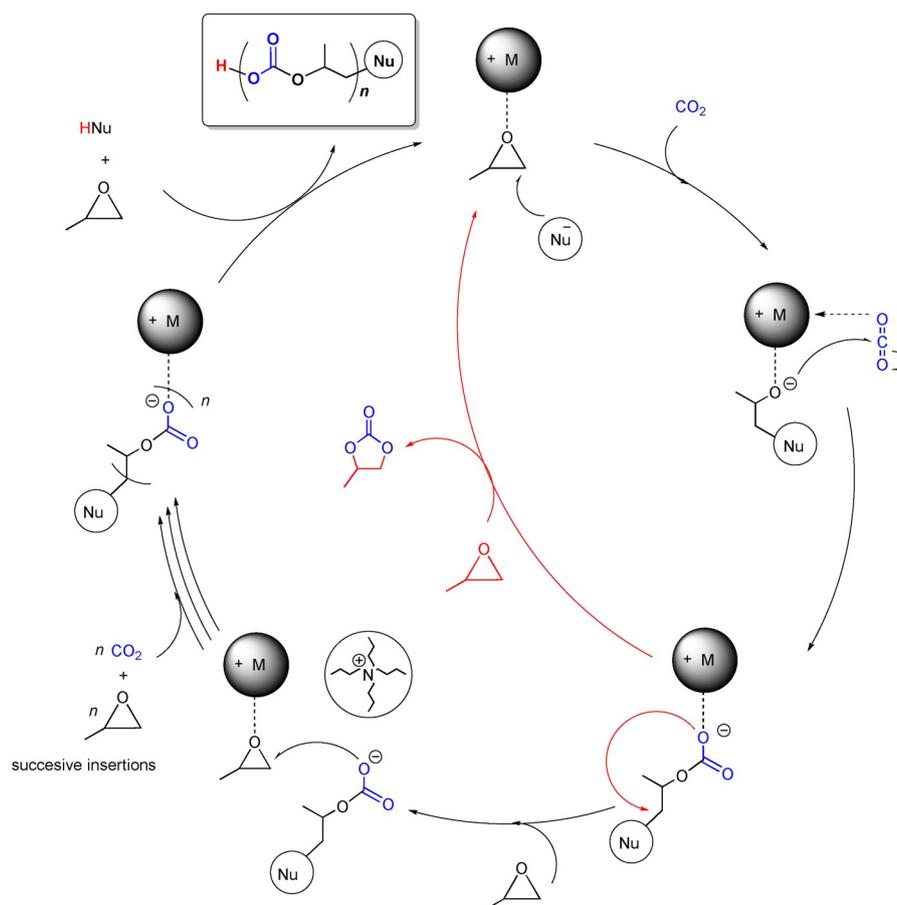
of the carbonate-metal species formed during the catalytic cycle.

Indeed, strong carbonate-metal bond should favor the back-biting process (red pathway, Scheme 4) thus leading to the formation of the cyclic carbonate and/or low molecular weight copolymers. In contrast, a weak carbonate-metal bond should allow a fast reaction with a new epoxide molecule and afford successive epoxide and carbon dioxide insertions, thus producing polypropylene carbonate polymer with high molecular weight. In this context, the introduction of methyl groups in *ortho*-position of the salicy-naphthalene ligands is expected to weaken the interaction between the incipient carbonate and the metal center, is crucial to obtain high selectivities.

Further studies to gain information on this effect are currently on going in our group.

Conclusion

This paper described the synthesis of new *ortho*-substituted naphthalene Co^{III} catalysts and their performance in the copolymerization reaction between CO₂ and propylene oxide. The systems complexes **7–10**/PPNCI provided high activities for CO₂/propylene oxide copolymerization and selectively produced very high molecular weight copolymers. The effect of the *ortho*-substituents was rationalized by the destabilization of the metal-carbonate intermediates that produces rapid and successive PO/CO₂ insertions, and thus improves the selectivity to the copolymer and increases the molecular weight of this product.



Scheme 4. Catalytic cycle for the CO₂/PO copolymerization catalyzed by cobalt(III)-salicy type complexes and a co-catalyst.

Their catalytic activity was increased by lowering the catalyst loading and diluting the system with hexane, which make them of interest for the industry in which low catalyst cost and low residues in the polymer are required for commercial purposes.

Experimental Section

General procedures

All the reagents were purchased in Aldrich and used as received. Methanol, ethanol and propylene oxide were dried over calcium hydride and distilled prior to its use. THF and dichloromethane were used directly from the solvent purified system Braun MB SPS-800. Hexane solvent from the same purified system was further dried under CaH₂ before using for the catalytic reactions. Deuterated solvents were purchased at Tracertec and used as received. Carbon dioxide (CO₂, CP grade 5.3 and SCF Grade, 99.995%) was supplied by Messer. Solution NMR spectra were obtained at the *Servei de Recursos Científics i Tècnics (SRCiT)* of the URV using a 400 MHz Varian Mercury VX400 spectrometer and calibrated to the residual solvent peaks and at the *Repsol Technology Center (CTR)* using a 500 MHz Bruker AV III HD 500 spectrometer.^[16] High resolution mass spectrometry (electrospray ionization-time-of-flight (ESI-TOF)) analyses were also performed at the *SCRiT* on an Agilent Time-of-Flight 6210 spectrometer. IR spectra (range 4000–400 cm⁻¹) were recorded on a Midac Grams/386 spectrometer in attenuated

total reflectance or KBr. Molecular weights and polydispersity index (M_w/M_n) were determined against polystyrene (PS) standards by gel-permeation chromatography (GPC) at the CTR using a Bruker 3800 equipped with a deflection refractive index detector. Tetrahydrofuran at 1 mL min⁻¹ flow rate was used as eluent at room temperature. The Schiff base ligands (±)-*N,N*-bis-(2-hydroxy-1-naphthaldehyd)-1,2-phenylenediimine **L1**^[13] and **L2**^[13a, 14] were synthesized as described previously in the bibliography. The Co^{III} complexes **1**,^[13] **2**,^[13] **3**,^[14, 15] **6**,^[14, 15] **11**,^[15] and **12**^[8b] have been synthesized following the procedures previously described in the literature.

Synthesis of 2-hydroxy-3-methyl-1-naphthaldehyde (b) and 3-ethyl-2-hydroxy-1-naphthaldehyde (c)

In a round flask was added MgCl₂ (2 equivalents), the corresponding naphthol compound (1 equivalent) and *para*-formaldehyde (5 equivalents) in dry THF over inert atmosphere. To this mixture, distilled trimethylamine (2 equivalents) was added and then, the reaction was refluxed at 90 °C overnight. Over this time, the mixture was cooled to room temperature and the solvent was evaporated over reduced pressure. The crude solid was dissolved in dichloromethane and HCl (10 mL, 10%). Then, the aqueous phase was extracted with dichloromethane. The organic extracts were washed carefully with a saturated solution of NaHCO₃ and were dried with anhydrous MgSO₄, filtered and finally, the solvent was evaporated to dryness. The crude was purified by column chroma-

tography in SiO₂ using a mixture of hexane/Et₂O (99:1, R_f=0.35) as eluent.

b: Yield = 19%; ¹H NMR (400 MHz, CDCl₃): δ = 2.36 (s, 3H, CH₃), 7.40 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, Ar-H), 7.55 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H, Ar-H), 7.74–7.68 (m, 1H, Ar-H), 7.80 (s, 1H, Ar-H), 8.28 (d, *J* = 8.4 Hz, 1H, Ar-H), 10.81 (s, 1H, CHO), 13.56 (br., 1H, OH); ¹³C{¹H}NMR (100.57 MHz, CDCl₃): δ = 16.13 (CH₃), 110.02 (C), 110.81(C), 118.32 (CH aromatic), 124.36 (CH aromatic), 127.61 (C), 128.07 (CH aromatic), 128.64 (CH aromatic), 131.90(Cq), 138.28 (CH aromatic), 164.53 (C), 193.31 (CHO).

c: Yield = 14%; ¹H NMR (400 MHz, CDCl₃): δ = 1.33 (t, *J* = 7.5 Hz, 3H, CH₂CH₃), 2.83 (dd, *J* = 7.5, 0.9 Hz, 2H, CH₂CH₃), 8.20 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.82 (s, 1H, Ar-H), 7.77–7.74 (m, 1H, Ar-H), 7.58–7.54 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H, Ar-H), 7.44–7.39 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, Ar-H), 10.81 (s, 1H, CHO), 13.60 (br., 1H, OH); ¹³C{¹H}NMR (100.57 MHz, CDCl₃): δ = 16.13 (CH₂CH₃), 22.67 (CH₂CH₃), 109.99 (C), 110.75(C), 118.21 (CH aromatic), 124.41 (CH aromatic), 126.29 (C), 128.14 (CH aromatic), 128.87 (CH aromatic), 129.13 (C), 136.69 (CH aromatic), 164.46 (C), 193.35 (CHO).

Synthesis of L3 and L4

The synthesis of these ligands was performed by condensation in ethanol overnight, as previously reported for other salen ligands. To a solution of the corresponding fragment 2-hydroxy-naftaldehyde (a–c) (1 mmol, 2 equiv) in warm ethanol was slowly added cyclohexane-1,2-diamine (0.5 mmol, 1 equiv). Then, the mixture was refluxed and stirred overnight. Once the reaction reached room temperature, the solvent was evaporated under reduced pressure and washed several times with cool ethanol. Finally, the solid was dried under vacuum overnight to yield **L3** or **L4** in quantitative yield.

L3: ¹H NMR (400 MHz, CDCl₃): δ = 1.50–1.44 (m, 2H, CH₂cy), 1.75–1.73 (m, 2H, CH₂cy), 1.99–1.92 (m, 2H, CH₂cy), 2.20 (s, 6H, CH₃), 2.24 (m, 2H, CH₂cy), 3.39–3.37 (m, 2H, CHcy), 7.11–7.08 (m, 2H, Ar-H), 7.26–7.21 (m, 2H, Ar-H), 7.37–7.34 (m, 4H, Ar-H), 7.65–7.63 (m, 2H, Ar-H), 8.63 (m, 2H, CH=N), 14.57 (br. s, 2H, OH); ¹³C{¹H}NMR (100.57 MHz, CDCl₃): δ = 174.38 (C-OH), 158.67 (CH=N), 135.75 (CH aromatic), 132.46 (C), 131.32 (C), 128.02 (CH aromatic), 127.01 (CH aromatic), 126.24 (C), 122.66 (CH aromatic), 117.84 (CH aromatic), 106.14 (C), 68.29 (CHcy), 32.61 (CH₂cy), 24.34 (CH₂cy), 16.35 (CH₃).

L4: ¹H NMR (400 MHz, CDCl₃): δ = 1.22 (t, 6H, CH₃et), 1.57 (m, 2H, CH₂cy), 1.78 (m, 2H, CH₂cy), 1.95 (m, 2H, CH₂cy), 2.20 (m, 2H, CH₂cy), 2.64 (m, 4H, CH₂), 3.41 (m, 2H, CH), 7.10 (m, 2H, CH aromatic), 7.21 (m, 2H, CH aromatic), 7.32 (m, 2H, CH aromatic), 7.40 (m, 2H, CH aromatic), 7.65 (m, 2H, CH aromatic), 8.67 (m, 2H, CH=N), 14.67 (br. s, 2H, OH); ¹³C{¹H}NMR (100.57 MHz, CDCl₃): δ = 173.52 (C-OH), 158.76 (CH=N), 136.73 (C), 133.65 (CH aromatic), 129.12 (C), 128.20 (CH aromatic), 126.71 (CH aromatic), 126.31 (C), 122.62 (CH aromatic), 117.81 (CH aromatic), 106.31 (C), 68.79 (CHcy), 32.81 (CH₂cy), 23.14 (CH₂cy), 22.81 (CH₂CH₃), 12.92 (CH₂CH₃).

Synthesis of cobalt complexes

Cobalt (II) precursors [Co(L)]: a solution of the ligand in dichloromethane was added under argon to a solution of cobalt acetate (1 equiv) in methanol. Immediately, a formation of a dark precipitated was observed. Then, the mixture was allowed to stir during 15 minutes at room temperature and subsequently at 0 °C during

half an hour. Finally, the solid was filtered, washed with cool methanol and dried under vacuum overnight.

[Co(L2)OTs] (**4**): A solution of the cobalt complex (II)-naphthalene in dichloromethane was stirred at room temperature under air in presence of 1.06 equivalents of the *p*-toluenesulfonic acid during 6 hours. Then, the solvent was evaporated and the residue was suspended in hexane, and then filtered and dried over vacuum overnight. The product was isolated as a dark brown solid in high yield (88%).

¹H NMR (400 MHz, [D₆]DMSO): δ = 1.62 (m, 2H, CH₂-Cy), 2.04 (m, 4H, CH₂-Cy), 2.24 (s, 3H, CH₃-TsO), 3.31 (m, 2H, CH₂-Cy), 3.86 (s, 2H, CH-Cy), 7.05 (d, 2H, OTs), 7.26 (pt, 2H, CH), 7.42 (d, 2H, OTs), 7.53 (pt, 2H, CH), 7.73 (d, 2H, CH), 7.81 (d, 2H, CH), 7.94 (d, 2H, CH), 8.22 (d, 2H, CH), 8.65 (s, 2H, CH=N); ¹³C{¹H} NMR (100.57 MHz, [D₆]DMSO): δ = 21.22 (CH₃, OTs), 24.82 (CH₂, Cy), 30.01 (CH₂, Cy), 71.11 (CH, Cy), 108.19 (C, aromatic), 120.62 (CH, aromatic), 122.78 (CH, aromatic), 125.36 (CH, aromatic), 125.93 (CH, OTs), 127.01 (CH, aromatic), 128.18 (CH, aromatic), 128.47 (CH, OTs), 129.17 (CH, aromatic), 134.46 (C, aromatic), 135.68 (CH, OTs), 137.97 (C, aromatic), 158.28 (CH=N), 166.67 (C, aromatic); ESI-TOF (*m/z*): 479.1184 (*M*⁺).

[Co(L2)NO₃] (**5**): To a solution of the complex **3** (157 mg, 0.30 mmol) in dichloromethane was added silver nitrate (54 mg, 0.32 mmol, 1.05 equiv). The mixture was stirred during 8 hours at room temperature protected from light. Then, the suspension was filtered over celite and the filtrate was evaporated to dryness under vacuum. The solid was suspended in hexane, filtered and dried under vacuum overnight (63% yield).

¹H NMR (400 MHz, [D₆]DMSO): δ = 1.23 (m, 2H, CH₂-Cy), 1.65 (m, 2H, CH₂-Cy), 2.07 (m, 4H, CH₂-Cy), 3.89 (s, 2H, CH-Cy), 7.29 (m, 2H, CH), 7.56 (m, 2H, CH), 7.77 (br s, 2H, CH), 7.84 (br s, 2H, CH), 7.96 (m, 2H, CH), 8.25 (m, 2H, CH), 8.67 (s, 2H, CH=N); ¹³C{¹H} NMR (100.57 MHz, [D₆]DMSO): δ = 24.84 (CH₂, Cy), 30.02 (CH₂, Cy), 71.13 (CH, Cy), 108.20 (C, aromatic), 120.63 (CH, aromatic), 122.80 (CH, aromatic), 125.37 (CH, aromatic), 127.03 (C, aromatic), 128.19 (CH, aromatic), 129.18 (CH, aromatic), 134.47 (C, aromatic), 135.69 (CH, aromatic), 158.29 (CH=N), 166.65 (C, aromatic). ESI-TOF (*m/z*): 479.1184 [*M*⁺].

[Co(L3)OAc] (**7**) and [Co(L4)OAc] (**9**): A solution of the cobalt complex (II)-naphthalene in dichloromethane was stirred at room temperature under air in presence of 2 equivalents of the acetic acid during 6 hours. Then, the solvent was evaporated and the residue was suspended in hexane, and then filtered and dried over vacuum overnight. The products were isolated as brown solids in high yield (75% **7**, and 87% **9**).

7: ¹H NMR (400 MHz, [D₆]DMSO): δ = 1.50 (s, 3H, CH₃-OAc), 1.61 (m, 2H, CH₂-Cy), 2.05 (m, 4H, CH₂-Cy), 2.68 (s, 3H, CH₃), 2.74 (s, 3H, CH₃), 3.24 (m, 2H, CH₂-Cy), 4.12 (s, 2H, CH-Cy), 7.19 (m, 2H, CH), 7.41 (m, 2H, CH), 7.69 (m, 4H, CH), 8.08 (m, 2H, CH), 8.56 (s, 2H, CH=N); ¹³C{¹H} NMR (100.57 MHz, [D₆]DMSO): δ = 18.34 (CH₃), 18.40 (CH₃), 24.45 (CH₃, OAc), 24.98 (CH₂, Cy), 29.87 (CH₂, Cy), 71.13 (CH, Cy), 107.26 (C, aromatic), 119.47 (CH, aromatic), 121.54 (CH, aromatic), 125.77 (C, aromatic), 126.02 (C, aromatic), 126.32 (CH, aromatic), 127.74 (CH, aromatic), 132.42 (CH, aromatic), 132.68 (C, aromatic), 133.66 (C, aromatic), 156.69 (CH=N), 166.62 (C, aromatic); ESI-TOF (*m/z*): 507.1481 [*M*⁺].

9: ¹H NMR (400 MHz, [D₆]DMSO): δ = 1.27 (t, 6H, CH₃), 1.44 (m, 2H, CH₂), 1.49 (m, 2H, CH₂), 1.59 (m, 2H, CH₂), 2.05 (m, 5H, CH₂, CH₃OAc), 3.08(m, 4H, CH₂), 3.73–4.20 (m, 2H, CH), 7.15 (m, 2H, CH), 7.40 (m, 2H, CH), 7.68–7.62 (m, 4H, CH), 8.06 (m, 2H, CH), 8.54 (m,

2H, CH=N); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.57 MHz, $[\text{D}_6]\text{DMSO}$): δ = 15.02 (CH_2CH_3), 24.42 (CH_3 , OAc), 24.75 (CH_2CH_3), 25.01 (CH_2 , Cy), 29.95 (CH_2 , Cy), 71.01 (CH, Cy), 107.12 (C, aromatic), 119.42 (CH, aromatic), 121.65 (CH, aromatic), 125.79 (C, aromatic), 126.12 (C, aromatic), 126.36 (CH, aromatic), 127.82 (CH, aromatic), 132.39 (CH, aromatic), 132.23 (C, aromatic), 133.58 (C, aromatic), 156.72 (CH=N), 166.75 (C, aromatic). ESI-TOF (m/z): 535.1789 (M^+).

[Co(L3)DNP] (**8**) and [Co(L4)DNP] (**10**): A solution of the cobalt complex (II)-naphthalene in dichloromethane was stirred at room temperature under air in presence of 1 equivalent of the dinitrophenol during 12 hours. Then, the solvent was evaporated and the residue was suspended in hexane, and then filtered and dried over vacuum overnight. The products were isolated as brown-green solids in high yield (83% **8**, and 82% **10**).

8: ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.65 (m, 2H, CH_2), 2.07 (m, 4H, CH_2), 2.81 (s, 6H, CH_3), 3.45 (m, 2H, CH_2), 3.92 (m, 2H, CH), 6.33 (m, 1H, CH-DNP), 7.24 (m, 2H, CH), 7.48 (m, 2H, CH), 7.74 (m, 4H, CH and CH-DNP), 7.87 (m, 2H, CH), 8.18 (m, 2H, CH), 8.67 (m, 2H, CH=N); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.57 MHz, $[\text{D}_6]\text{DMSO}$): δ = 18.37 (CH_3), 24.96 (CH_2 , Cy), 29.82 (CH_2 , Cy), 71.18 (CH, Cy), 107.85 (C, aromatic), 121.02 (CH, aromatic), 122.58 (CH, aromatic), 126.01 (CH, aromatic), 126.78 (CH, aromatic), 127.12 (C, aromatic), 128.17 (CH, aromatic), 132.22 (CH, aromatic), 133.75 (C, aromatic), 138.71 (C, aromatic), 158.11 (CH=N), 165.28 (C, aromatic); ESI-TOF (m/z): 507.1475 [M^+].

10: ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.21 (m, 2H, CH_2), 1.59 (t, J = 7.4 Hz, 6H, CH_3), 1.65 (m, 2H, CH_2), 2.05 (m, 4H, CH_2), 3.28 (q, J = 7.4 Hz, 4H, CH_2), 3.90 (m, 2H, CH), 6.28 (m, 1H, CH DNP), 7.23 (m, 2H, CH), 7.46 (m, 2H, CH), 7.72 (m, 3H, 2xCH, 1 CH DNP), 7.86 (m, 2H, CH), 8.16 (m, 2H, CH), 8.65 (m, 3H, 1xCH DNP, 2xCH=N); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.57 MHz, $[\text{D}_6]\text{DMSO}$): δ = 14.66 (CH_2CH_3), 24.68 (CH_2CH_3), 25.14 (CH_2 , Cy), 29.87 (CH_2 , Cy), 71.19 (CH, Cy), 107.79 (C, aromatic), 120.25 (CH, aromatic), 122.77 (CH, aromatic), 125.59 (CH, aromatic), 126.98 (CH, aromatic), 127.24 (C, aromatic), 128.61 (CH, aromatic), 132.84 (CH, aromatic), 133.53 (C, aromatic), 138.77 (C, aromatic), 158.37 (CH=N), 165.62 (C, aromatic); ESI-TOF (m/z): 535.1789 [M^+].

Autoclave experiments

The copolymerization tests were performed in a 100 mL Berghoff autoclave reactor. The autoclave was introduced in the glovebox prior to use after 12 h over vacuum. In the glovebox, the batch reactor was filled with the catalyst, co-catalyst and PO in desired ratio. The reactor was sealed and outside of the glovebox was filled with CO_2 at the previous selected pressure and heated to the desired temperature. When the reaction time was over, the reactor was cooled down in an ice bath and subsequently CO_2 was released slowly. Then, a sample of crude reaction mixture was taken for ^1H NMR test to evaluate the selectivity of the reaction. The crude was poured in dichloromethane, and methanol was added to precipitate the copolymer. The crude was evaporated over vacuum until constant weight to determine the productivity and yield of the reaction.

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Conflict of interest

The authors declare no conflict of interest.

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