

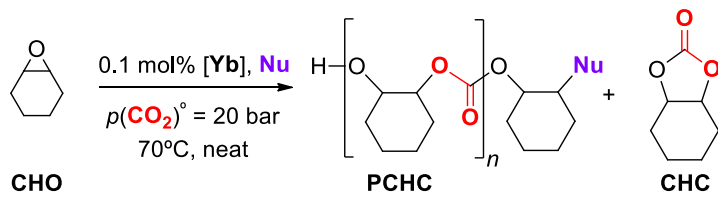
This document is the Accepted Manuscript version of a Published Work that appeared in final form in Macromolecular copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see [insert ACS Articles on Request authordirected link to Published Work, see <http://pubs.acs.org/doi/abs/10.1021/acs.macromol.5b01880>

]”Copolymerization of CO<sub>2</sub> and Cyclohexene Oxide Mediated by Yb(salen) Based Complexes  
*Antonello Decortes,<sup>†</sup> Robert M. Haak,<sup>†</sup> Carmen Martín,<sup>†</sup> Marta Martínez Belmonte,<sup>†</sup> Eddy  
Martin,<sup>†</sup> Jordi Benet-Buchholz,<sup>†</sup> Arjan W. Kleij<sup>\*,†,‡</sup>*

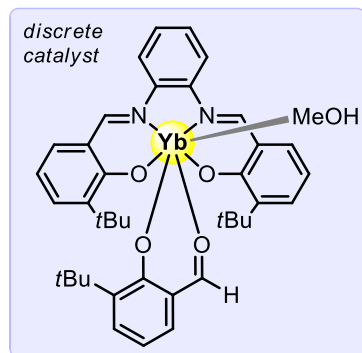
<sup>†</sup>Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 – Tarragona,  
Spain.

<sup>‡</sup>Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 –  
Barcelona, Spain.

**Table of contents entry:**



- PCHC:CHC selectivity >99:1
- >99% carbonate linkages
- $M_n$  up to 11 kD, PDI 1.3-1.4
- average TOF up to  $31 \text{ h}^{-1}$



**ABSTRACT:** New catalysts based on Yb(salen) complexes active for the copolymerization of cyclohexene oxide (CHO) and CO<sub>2</sub> to give poly(cyclohexene)carbonate (PCHC) are reported. In combination with co-catalytic, nucleophilic chloride additives these new (binary) catalysts provided good conversion and selectivity for PCHC formation with average turnover frequencies of up to 35 h<sup>-1</sup> and narrow molecular weight distributions. The best results were obtained with the binary catalyst system **1** (0.1 mol%)/NBu<sub>4</sub>Cl (0.05 mol%), and at 90 °C a conversion of 57% was reached after 18 h with a TOF of 31 h<sup>-1</sup>, and the polycarbonate had an M<sub>n</sub> of 10.2 Kg/mol and a PDI of 1.54. Comparative catalysis studies have also been performed with a series of literature systems based on transition metal/lanthanide salen complexes, and the newly presented catalysts show comparatively good activity as well as copolymerization selectivity. MALDI-ToF mass spectrometric analysis revealed that trace water contamination and/or traces of 1,2-cyclohexane-diol were responsible for chain transfer effects limiting to some extent the maximum molecular weights that can be achieved in the current reactor set up.

## INTRODUCTION

In recent years, reactions using carbon dioxide as starting material have been the focus of increasing research efforts.<sup>1</sup> Amongst the numerous reported transformations, reactions of CO<sub>2</sub> with epoxides to produce either cyclic<sup>2</sup> or poly-carbonates have received special attention due to the industrial and economic importance of these products.<sup>3</sup> Among the catalysts used for such and related processes, salen-type trivalent cobalt and chromium complexes are especially prominent.<sup>4</sup> Other metal complexes that have been reported to successfully mediate the copolymerization of epoxides and CO<sub>2</sub> include, for instance, aluminum,<sup>5</sup> zinc,<sup>6</sup> magnesium,<sup>7</sup> iron<sup>8</sup> and manganese.<sup>9</sup> A limited number of homogeneous catalysts based on rare earth metals have been described for the copolymerization of epoxides and carbon dioxide. Hultsch and coworkers, for example, have developed catalysts based on lanthanum and yttrium ions supported by  $\beta$ -diketimate ligands,<sup>10</sup> whereas Hou and coworkers reported on cyclopentadienyl-ligated yttrium, dysprosium, lutetium and scandium catalysts.<sup>11</sup> The group of Cui reported catalysts based on yttrium, lutetium and scandium catalysts with  $\beta$ -diimine ligands.<sup>12</sup> It should also be noted that lanthanide based catalysts have previously also been applied as catalysts in the formation of other types of related copolymers such as those incorporating epoxides and/or cyclic anhydrides or lactides.<sup>13</sup>

To the best of our knowledge, the combination of rare-earth metals and salen-type ligands has not been explored in great detail for the coupling reaction between epoxides and CO<sub>2</sub> to afford polycarbonates. Therefore, our primary aim was to develop catalysts active towards this

copolymerization reaction and to study their catalytic efficiencies and polymer-derived products. A key aspect to control with these lanthanide based salen-type complexes is their strong aggregation behavior mediated by bridging ligands. The formation of mononuclear complexes is hence clearly preferred if catalytic applications are pursued. Here we describe these efforts and a simple, one-pot synthetic procedure has been developed that allows for the isolation a small series of discrete mononuclear Yb(salen) complexes with a pendant, hemi-labile phenoxide ligand. These complexes have been tested in the copolymerization of cyclohexene oxide (CHO) and CO<sub>2</sub> giving rise to polycarbonates with high selectivity control. A detailed comparison of the activity and selectivity of these systems with known literature catalysts under similar reaction conditions allowed for a realistic estimate of the activity and selectivity profiles of the newly presented Yb complexes.

## EXPERIMENTAL SECTION

**General comments:** Unless otherwise stated, all manipulations were carried out using standard Schlenk vacuum line techniques under a N<sub>2</sub> atmosphere or using a nitrogen-filled glove box. Starting materials were obtained from Aldrich and used as received unless stated otherwise. PPNCl (PPN = bis(triphenylphosphine)iminium), NBu<sub>4</sub>Cl and DMAP (4-dimethylamino-pyridine) were obtained from Aldrich and dried under vacuum at 80 °C or at room temperature (DMAP) overnight. PPNBr, PPNI, PPNN<sub>3</sub> and PPN(OAc) were prepared according to literature procedures.<sup>14,15</sup> Complexes **5**, **6** and **9-12** were prepared according to published procedures.<sup>16-18</sup> CHO and C<sub>6</sub>D<sub>6</sub> were dried over CaH<sub>2</sub>, distilled under reduced pressure and stored under a nitrogen atmosphere before use. Cyclohexanol was distilled over CaO prior to use. Commercial

CO<sub>2</sub> was obtained from Praxair and used without further purification. Solvents were dried by passing them through dried alumina towers and stored under nitrogen atmosphere.

Elemental analyses was performed by the Unidad de Análisis Elemental at the Universidad de Santiago de Compostela (Spain). Mass spectrometric analyses (MALDI-ToF mass for polymer and MALDI(+) and MALDI(-)-MS for new complexes) studies were carried out by the Research Support Group at the ICIQ using a BRUKER Autoflex matrix assisted laser desorption ionization (MALDI) time-of-flight mass spectrometer. Typical solutions of 1 mg/mL were prepared in dichloromethane using dithranol (10 mg/mL THF) as matrix and NaAcO (1 mg/mL MeOH) as additive. Samples were prepared by taking 5  $\mu$ L of analyte and combining it with 25  $\mu$ L of matrix and 1  $\mu$ L of additive.

FT-IR measurements were performed on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beam-splitter at 4 cm<sup>-1</sup> resolution. UV-Vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with a photomultiplier detector, double beam optics, and D2 and W light sources. NMR spectra were recorded on a Bruker AV-400 spectrometer and referenced to the residual NMR solvent signals.

Size exclusion chromatography (SEC/GPC) was measured on a Waters Alliance system equipped with a Waters 2695 separation module, a Waters 2414 refractive index detector (35 °C), a Waters 2487 dual absorbance detector, and a PSS SDV 5 m guard column followed by two PSS SDV linear XL columns in series of 5 m (8  $\times$  300) at 40 °C. THF stabilized with BHT (Biosolve) with 1% v/v acetic acid was used as eluent at a flow rate of 1.0 mL·min<sup>-1</sup>. The molecular weights were calculated with respect to polystyrene standards (Polymer Laboratories,  $M_p = 580$  Da up to  $M_p = 7.1 \times 10^6$  Da).

**X-ray crystallographic studies:** X-ray diffraction studies were carried out by the Research Support Group at the ICIQ. Crystals for the diffraction studies were prepared under inert conditions and immersed in perfluoro-polyether as protecting oil for further manipulation. Data Collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4 K CCD area detector, a FR591 rotating anode with Mo-K $\alpha$  radiation, Montel mirrors as mono-chromator and a Kryoflex low temperature device (T = -173 °C). Full-sphere data collection was used with  $\omega$  and  $\varphi$  scans. Programs used: data collection Apex2 V2009.1-0 (Bruker-Nonius 2009), data reduction Saint+ V7.60A (Bruker-Nonius 2009) and absorption correction SADABS Version 2008/1. In the case of twinned crystals, TWINABS Version 2008/4 Bruker AXS was applied.<sup>19</sup> Structure Solution and Refinement: this was performed with SHELXTL Version 6.14 (Sheldrick, 2008).<sup>20</sup>

**Synthesis of complexes 1–4:** In a typical experiment, the appropriate diamine (0.91 mmol) and Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (1.00 mmol) were mixed together in MeOH (15 mL). Upon complete dissolution, the respective salicylaldehyde (2.93 mmol) was added together with NEt<sub>3</sub> (4.55 mmol). A yellow precipitate readily formed and the resulting suspension was left to stir at reflux temperature for 3 hours. Afterwards, the reaction was allowed to cool down to r.t. and stirred for another 3 hours. Finally, the suspension was filtered and the resulting residue was washed with MeOH (three times) before it was dried under vacuum. In the case of complexes **1** and **4**, crystals were obtained by slow evaporation of the mother liquor left after isolation of the first fraction of product, and analyzed by single crystal X-ray diffraction. In general, the isolated Yb complexes were manipulated and characterized without any special precautions.

**Complex 1:** Yellow solid. Yield: 60%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, RT, paramagnetic spectrum):  $\delta$  = 32.17, 24.54, 18.29, 15.29, 15.05, 13.13, 12.52, 10.32, 8.59, 7.58, 3.73, 3.31,

1.94, 1.41, 0.76, -1.58, -2.64, -3.20, -3.72, -9.90; MS (MALDI+, pyrene):  $m/z = 777.4$  [M – MeOH]<sup>+</sup> (calcd. 777.3), 825.4 [M + H<sub>2</sub>O – H]<sup>+</sup> (calcd. 825.4). HRMS (MALDI+, dctb): found;  $m/z = 777.2590$  [M – MeOH]<sup>+</sup> (calcd. 777.2611); Anal. calcd. for C<sub>39</sub>H<sub>43</sub>N<sub>2</sub>O<sub>4</sub>Yb·MeOH: C 59.40, H 5.86, N 3.46; found: C 59.18, H 6.27, N 3.41. IR (cm<sup>-1</sup>):  $\nu = 3531, 2944, 2902, 2854, 2774, 1629, 1610, 1581, 1535, 1428, 1409, 1385, 1329, 1319, 1183, 1141, 1084, 1006, 869, 753, 640, 531, 486$ ; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>, 0.04 mM, 25 °C,  $\epsilon = \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ):  $\lambda = 281 \text{ nm (29850), 296 nm (31025), 382 (25300)}$ .

**Complex 2:** Yellow solid. Yield: 67%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, RT, paramagnetic spectrum):  $\delta = 13.77, 11.72, 9.80, 8.18, 7.14, 6.88, 6.61, 3.98, 3.23, 1.78, 1.30, -15.17$ ; MALDI(+) (dctb):  $m/z = 783.4$  [M – MeOH]<sup>+</sup> (calcd. 783.3). HRMS (MALDI+, pyrene):  $m/z = 783.2893$  [M – MeOH]<sup>+</sup> (calcd. 783.3081); Anal. calcd. for C<sub>39</sub>H<sub>49</sub>N<sub>2</sub>O<sub>4</sub>Yb·4H<sub>2</sub>O: C 54.79, H 6.72, N 3.28; found: C 54.66, H 6.67, N 3.20. IR (cm<sup>-1</sup>):  $\nu = 3529, 2945, 2905, 2868, 1629, 1610, 1535, 1409, 1385, 1329, 1184, 1141, 1084, 870, 753, 640$ ; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>, 0.04 mM, 25 °C,  $\epsilon = \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ):  $\lambda = 268 \text{ nm (29480), 354 nm (12860)}$ .

**Complex 3:** Yellow solid. Yield: 68%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, RT, paramagnetic spectrum):  $\delta = 37.97, 32.59, 22.20, 17.99, 15.91, 14.17, 13.73, 11.69, 10.93, 9.78, 8.33, 4.33, 3.75, 1.55, 1.35, -2.57, -3.66, -4.13, -5.49, -15.23, -19.90$ ; MALDI(+) (dctb):  $m/z = 722.4$  [M – MeOH – salicylaldehyde]<sup>+</sup> (calcd. 722.2), 916.5 [M – MeOH – H + 2H<sub>2</sub>O]<sup>+</sup> (calcd. 916.3). HRMS (MALDI+, pyrene):  $m/z = 722.2346$  [M – MeOH – salicylaldehyde + H<sub>2</sub>O]<sup>+</sup> (calcd. 722.2429). Anal. calcd. for C<sub>36</sub>H<sub>38</sub>N<sub>2</sub>O<sub>2</sub>Yb·2MeOH·2H<sub>2</sub>O: C 56.78, H 6.27, N 3.48; found: C 56.35, H 6.00, N 3.70. IR (cm<sup>-1</sup>):  $\nu = 3331, 3280, 2948, 2904, 2867, 1627, 1598, 1538, 1431, 1406, 1337, 1186, 1141, 1059, 980, 871, 753, 696, 543, 438$ ; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>, 0.04 mM, 25 °C,  $\epsilon = \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ):  $\lambda = 273 \text{ nm (19550), 375 nm (11675)}$ .



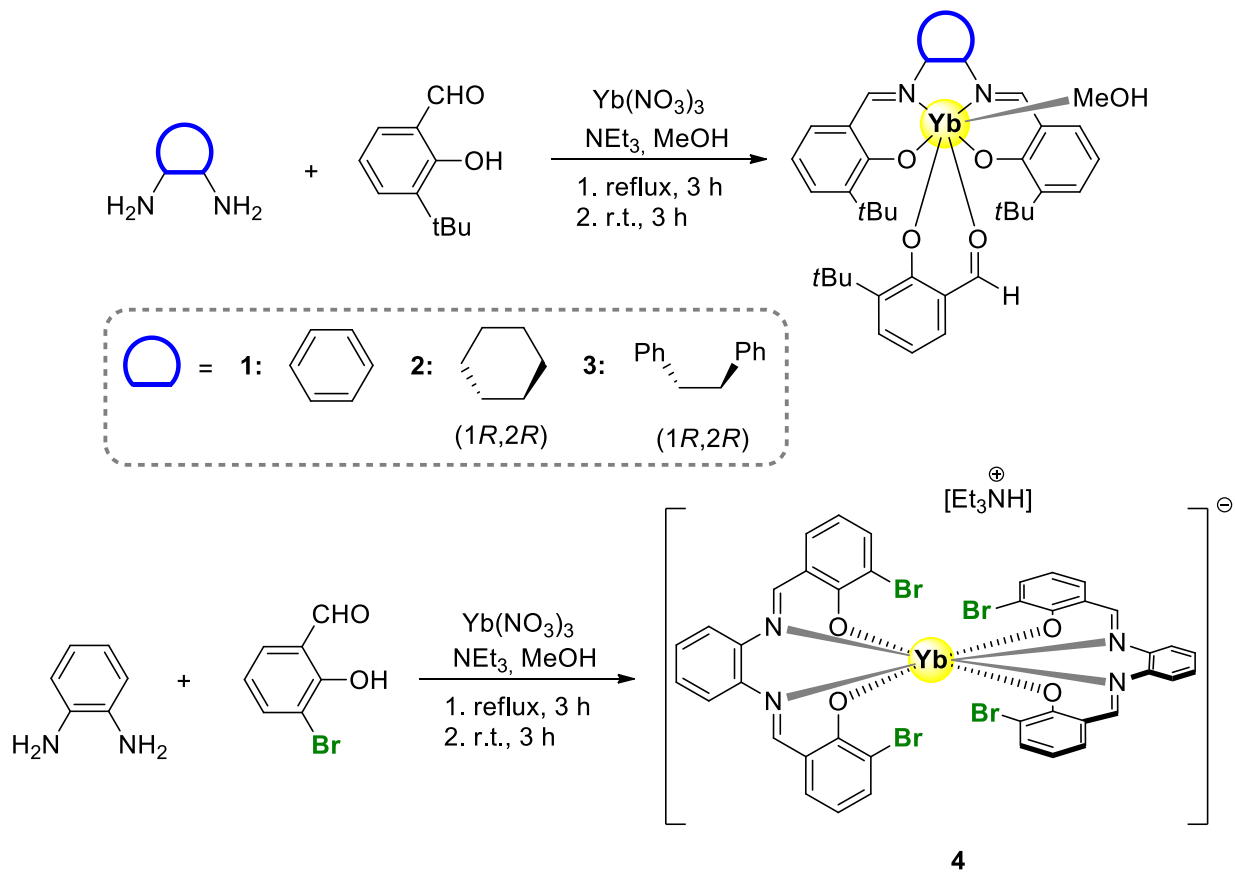
**Complex 4:** Yellow solid. Yield: 43%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, RT, paramagnetic spectrum):  $\delta = 34.66, 30.85, 21.60, 4.36, 1.12, 0.98, -2.36, -2.89$ ; MALDI(+) (pyrene):  $m/z = 1117.8$  ( $\text{M} - \text{NEt}_3\text{H}^+$ ) (calcd. 1117.8). HRMS (MALDI-, pyrene):  $m/z = 1117.7965$  [ $\text{M} - \text{NEt}_3\text{H}^+$ ] (calcd. 1117.7879). Anal. calcd. for  $\text{C}_{46}\text{H}_{40}\text{Br}_4\text{N}_5\text{O}_4\text{Yb}\cdot 5\text{H}_2\text{O}$ : C 42.19, H 3.85, N 5.35; found: C 42.55, H 3.30, N 4.97. IR ( $\text{cm}^{-1}$ ):  $\nu = 3049, 2988, 2890, 1605, 1577, 1516, 1442, 1387, 1202, 1170, 1124, 1070, 839, 750, 737, 655, 453$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ , 0.04 mM, 25 °C,  $\epsilon = \text{L}\cdot\text{mol}^{-1}\cdot\text{m}^{-1}$ ):  $\lambda = 292 \text{ nm} (9575), 324 \text{ nm} (13000), 375 (16125)$ .

**Synthesis of complexes 7 and 8:** Complexes **7** and **8** were prepared by stirring a mixture of **5** or **6** (0.1 mmol) and dry cyclohexanol (0.1 mmol) in DCM (5 mL) for 24 hours, followed by removal of the solvent *in vacuo* and drying of the resulting residue for a few hours under reduced pressure to give a yellow powder. The disappearance of the septet at 4.82 ppm (for **5**) and 4.96 ppm (for **6**) and the simultaneous appearance of a broad singlet at 3.71 and 4.07 ppm, respectively, demonstrated the formation of **7** and **8**. Complex 7:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.70$  (s, 1H, CH=N), 7.65 (s, 1H, CH=N), 7.56 (d, 2H, aryl-H), 6.99 (d, 2H, aryl-H), 3.71 (m, 1H,  $\text{C}_5\text{H}_{10}\text{-CH-O}$ ), 3.47 (dd, 2H,  $\text{N}(\text{CH}_2)_2\text{N}$ ), 2.71 (dd, 2H,  $\text{N}(\text{CH}_2)_2\text{N}$ ), 1.68 (s, *t*Bu), 1.38 (s, *t*Bu), 1.59-1.41 (m, cyclohexyl-H). Complex 8:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.79$  (s, 2H, CH=N), 7.68 (d, 2H, aryl-H), 7.06 (d, 2H, aryl-H), 4.07 (br s, 1H,  $\text{C}_5\text{H}_{10}\text{-CH-O}$ ), 3.86 (br s, 4H, thf), 3.56 (br s, 4H,  $\text{N}(\text{CH}_2)_2\text{N}$ ), 2.74 (br s, 4H, thf), 1.67 (s, 18H,  $\text{CH}_3$ ), 1.40 (s, 18H,  $\text{CH}_3$ ), 1.50-1.25 (m, cyclohexyl-H).

**General catalytic procedure for the copolymerization of  $\text{CO}_2$  and CHO:** In a typical experiment, the catalyst (0.02 mmol), co-catalyst (0.02 mol) and CHO (2.0 mL, 19.77 mmol) were added inside a glove box into the teflon reaction vessel (a 25 mL stainless-steel Berghof autoclave) which had been previously dried *in vacuo* for 18 h at 140 °C. Three cycles of

pressurization and depressurization of the reactor (with CO<sub>2</sub> at 10 bar) were carried out before finally stabilizing the pressure at 20 bar and the solution left stirring at the appropriate temperature for 18h. After the reaction was stopped, the autoclave was allowed to cool down to room temperature before it was vented. The crude reaction mixture was analyzed by <sup>1</sup>H NMR and FT-IR spectroscopy to determine the conversion to polymer, ether linkages and cyclic carbonate.

**Isolation of the polymers:** The crude reaction mixture was extracted with dichloromethane and the solution allowed evaporating. This unpurified mixture was then re-dissolved in a minimal amount of dichloromethane and the polymer precipitated with a 1 M solution of hydrochloric acid in methanol. Upon settling, the supernatant solution containing catalyst, co-catalyst and cyclic carbonate was decanted and discarded. The obtained purified polymer was dried *in vacuo* at 60 °C overnight and analyzed by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR, IR, MS (MALDI+) and GPC.

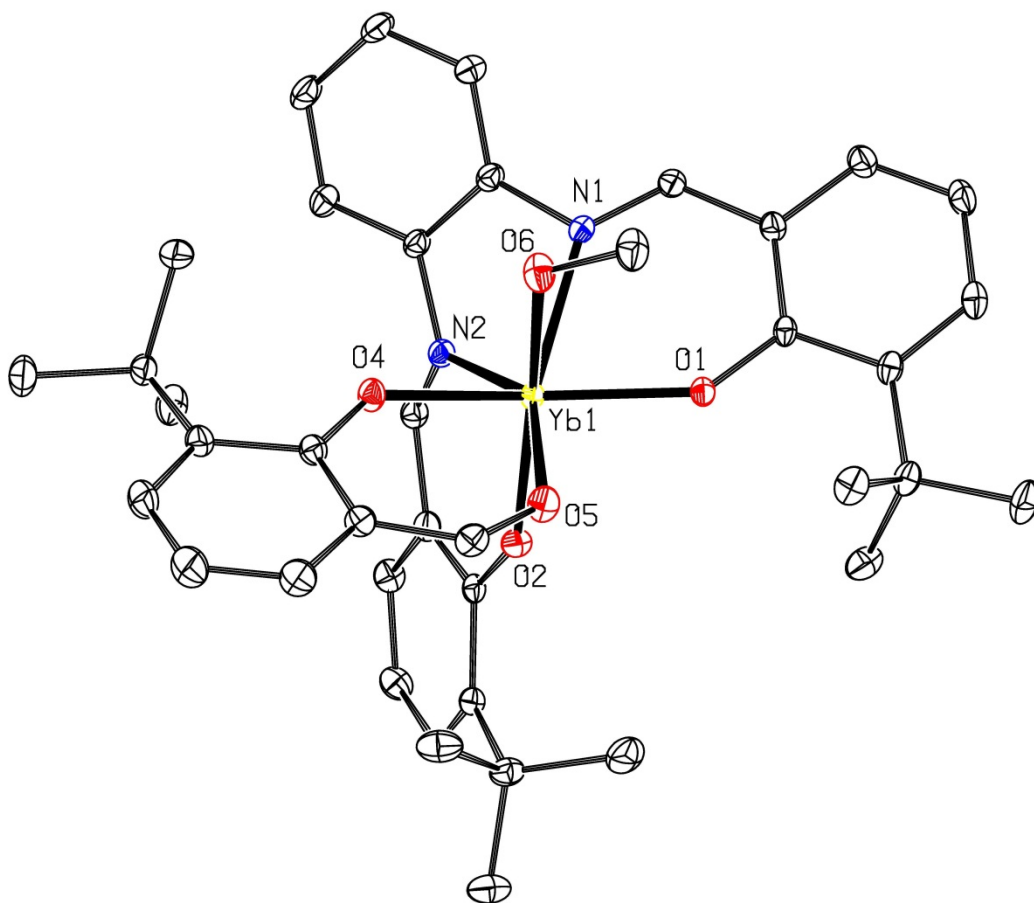


**Scheme 1.** Synthetic route for the synthesis of the Yb(salen) complexes **1–4**.

## RESULTS AND DISCUSSION

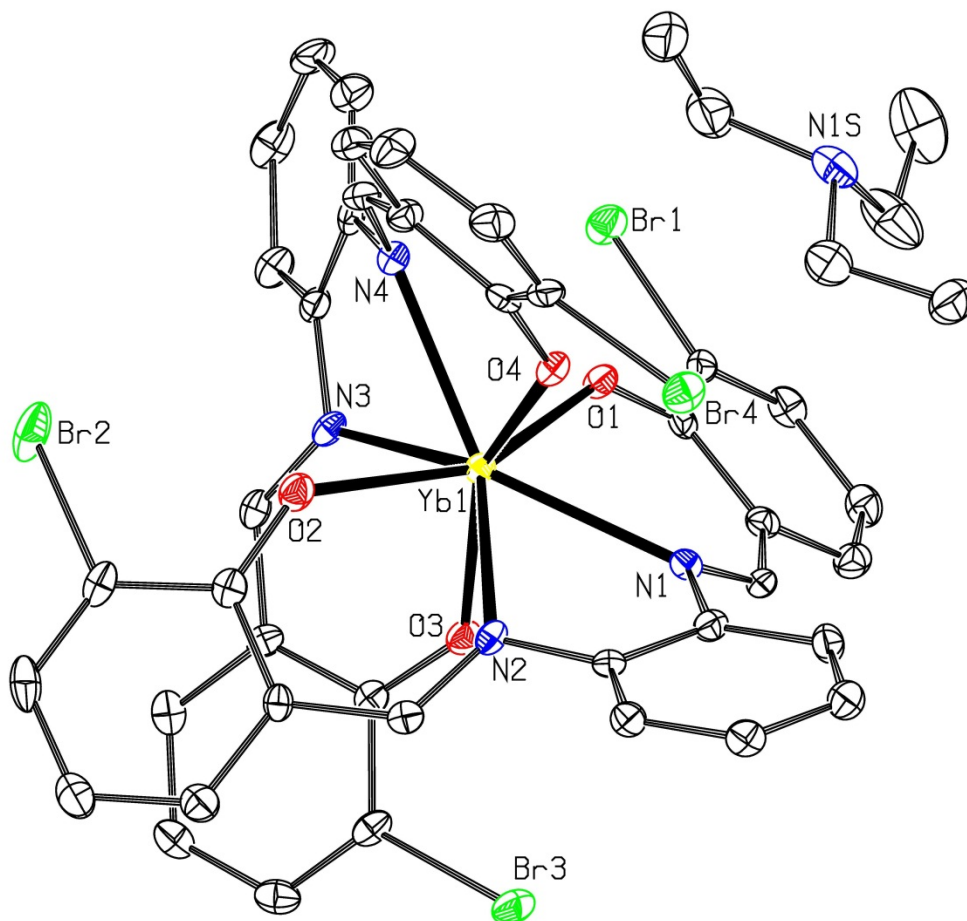
**Preparation and analysis of complexes:** A small number of complexes based on ytterbium (**1–4**, see Scheme 1) have been prepared. The synthetic approach is based on the combination of a mixture of an appropriate diamine, 3-R-butylsalicylaldehyde [R = *t*Bu (for **1–3**) or Br (for **4**)] and ytterbium nitrate in an approximate 1:3:1 ratio in methanol in the presence of triethylamine. It is noteworthy that this one-pot synthesis reproducibly leads to discrete monometallic ytterbium complexes. If the reaction is performed with pre-formed salen or salphen ligands and combined with Yb(NO<sub>3</sub>)<sub>3</sub> under comparable reaction conditions, only catalytically inactive polymeric material is produced. Apparently in the latter cases the isolated products are based on multinuclear Yb complexes incorporating bridging ligands, which is a common feature encountered in lanthanide chemistry. Complexes **1–4** were isolated in reasonably good yields of up to 68%.

Complexes **1** and **4** were first analyzed by single crystal X-ray crystallography (see Figures 1 and 2). Pertinent bond lengths and angles are collected in the Figure's legends, whereas crystal data/parameters are summarized in Table 1. The substitution on the aldehyde reagent in the 3-position determines the nature of the complex that is formed. In the case of complex **1**, having a bulky *t*Bu group, a mononuclear Yb(III)-salen complex is formed in which a deprotonated salicylaldehyde fragment (cf, a formyl-phenolate ligand) is coordinating to the metal center in a bidentate fashion. The seven-membered coordination sphere around Yb(1) is completed by a neutral MeOH molecule giving rise to a distorted pentagonal bipyramidal geometry. The bidentate coordination of the formyl-phenolate may be regarded as hemi-labile which may be of use in catalytic applications. Also, the neutral MeOH ligand could potentially be displaced by other, appropriate initiating species (cf., copolymerization reactions, *vide infra*).



**Figure 1.** Molecular structure for Yb-complex **1**. Hydrogen atoms are omitted for clarity.

Selected bond lengths (Å) and angles (°) with esd's in parentheses: Yb(1)-O(1) = 2.1521(11), Yb(1)-O(2) = 2.1394(13), Yb(1)-O(4) = 2.1804(12), Yb(1)-O(5) = 2.3314(12), Yb(1)-O(6) = 2.3871(15), Yb(1)-N(1) = 2.3999(13), Yb(1)-N(2) = 2.4218(14); O(2)-Yb(1)-O(1) = 96.83(5), O(2)-Yb(1)-O(4) = 95.43(5), O(1)-Yb(1)-O(4) = 158.27(5), O(2)-Yb(1)-O(5) = 83.78(5), O(1)-Yb(1)-O(5) = 87.10(5), O(5)-Yb(1)-O(6) = 76.54(5), N(2)-Yb(1)-O(5) = 147.97(5), N(2)-Yb(1)-O(4) = 82.36(5), N(1)-Yb(1)-O(5) = 145.63(5), N(1)-Yb(1)-O(4) = 112.56(5), N(1)-Yb(1)-N(2) = 65.30(5).



**Figure 2.** Molecular structure for Yb-complex **4**. Hydrogen atoms and co-crystallized  $\text{HNEt}_3\text{NO}_3$  molecules are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with esd's in parentheses:  $\text{Yb}(1)\text{-O}(1) = 2.202(2)$ ,  $\text{Yb}(1)\text{-O}(2) = 2.221(2)$ ,  $\text{Yb}(1)\text{-O}(3) = 2.2161(19)$ ,  $\text{Yb}(1)\text{-O}(4) = 2.2211(19)$ ,  $\text{Yb}(1)\text{-N}(1) = 2.488(2)$ ,  $\text{Yb}(1)\text{-N}(2) = 2.502(2)$ ,  $\text{Yb}(1)\text{-N}(3) = 2.526(2)$ ,  $\text{Yb}(1)\text{-N}(4) = 2.478(2)$ ;  $\text{O}(1)\text{-Yb}(1)\text{-O}(2) = 150.49(8)$ ,  $\text{O}(3)\text{-Yb}(1)\text{-O}(4) = 150.61(7)$ ,  $\text{N}(1)\text{-Yb}(1)\text{-N}(3) = 136.58(7)$ ,  $\text{N}(2)\text{-Yb}(1)\text{-N}(4) = 135.68(8)$ ,  $\text{O}(1)\text{-Yb}(1)\text{-O}(3) = 91.79(7)$ ,  $\text{O}(2)\text{-Yb}(1)\text{-O}(4) = 92.67(7)$ ,  $\text{O}(1)\text{-Yb}(1)\text{-N}(1) = 72.99(7)$ ,  $\text{O}(2)\text{-Yb}(1)\text{-N}(2) = 71.09(8)$ ,  $\text{N}(1)\text{-Yb}(1)\text{-N}(2) = 65.32(8)$ ,  $\text{N}(3)\text{-Yb}(1)\text{-N}(4) = 65.10(8)$ .

**Table 1.** Crystal data for complexes **1** and **4**.

	<u>Complex 1:</u>	<u>Complex 4:</u>
Empirical formula	C <sub>40</sub> H <sub>47</sub> N <sub>2</sub> O <sub>5</sub> Yb	C <sub>58</sub> H <sub>72</sub> Br <sub>4</sub> N <sub>9</sub> O <sub>10</sub> Yb
Formula weight	808.84	1547.93
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	<i>P</i> 2(1)2(1)2(1)	<i>P</i> 2(1)/n
Unit cell dimensions	<i>a</i> = 13.3478(4) Å <i>b</i> = 15.5479(4) Å <i>c</i> = 17.2278(5) Å	<i>a</i> = 16.2698(11) Å <i>b</i> = 15.1873(9) Å <i>c</i> = 25.1775(16) Å
Unit cell angles	$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \gamma = 90^\circ$ $\beta = 96.682(2)^\circ$
Volume	3575.29(18) Å <sup>3</sup>	6179.0(7) Å <sup>3</sup>
<i>Z</i>	4	4
Density (calculated)	1.503 Mg/m <sup>3</sup>	1.664 Mg/m <sup>3</sup>
Absorption coefficient	2.662 mm <sup>-1</sup>	4.163 mm <sup>-1</sup>
<i>F</i> (000)	1644	3092
Crystal size	0.15 × 0.15 × 0.15 mm <sup>3</sup>	0.40 × 0.05 × 0.05 mm <sup>3</sup>
$\theta$ range for data collection	2.33–37.04°	1.57–30.14°
Reflections collected	56735	39318
Independent reflections	18177 [ <i>R</i> <sub>(int)</sub> = 0.0509]	15248 [ <i>R</i> <sub>(int)</sub> = 0.0363]
Completeness to $\theta = 30.14^\circ$	99.8%	83.5%

Absorption correction	Empirical	Empirical
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	18177/0/444	15248/0/748
Goodness-of-fit on $F^2$	1.02	1.019
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0248$ , $wR_2 = 0.0606$	$R_1 = 0.0325$ , $wR_2 = 0.0649$
R indices (all data)	$R_1 = 0.0265$ , $wR_2 = 0.0616$	$R_1 = 0.0511$ , $wR_2 = 0.0706$
Flack parameter	$x = -0.026(4)$	–
Largest diff. peak and hole	1.816 and $-0.625 \text{ e} \cdot \text{\AA}^{-3}$	0.915 and $-0.645 \text{ e} \cdot \text{\AA}^{-3}$

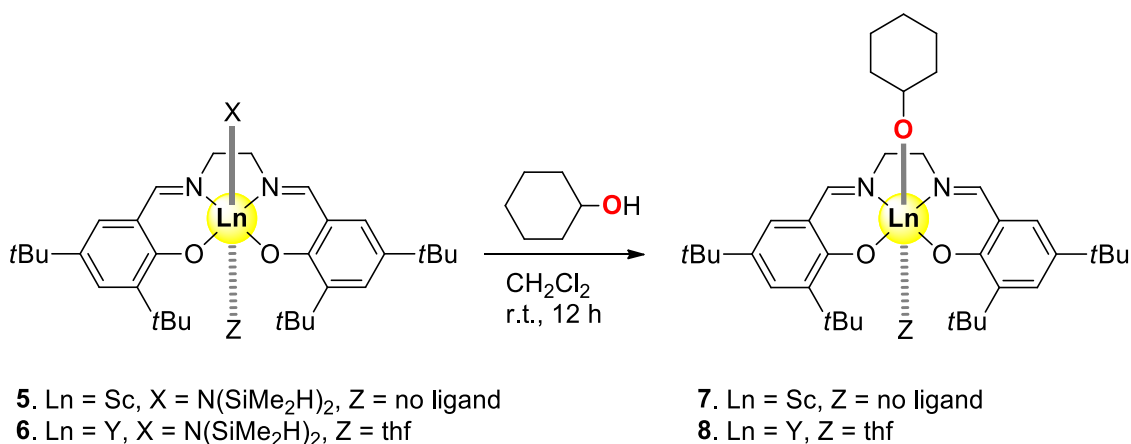
---

In complex **4**, the presence of a less bulky substituent in the aldehyde reagent (R = Br, Scheme 1) also leads to discrete formation of a mononuclear Yb complex, however in this case two dianionic *salphen* units are found in the coordination sphere of the metal ion with both acting as tetradentate ligands wrapped around the Yb center in a rather symmetrical fashion giving a square antiprismatic geometry. Due to the anionic nature of the complex a charge-compensating HNEt<sub>3</sub> cation co-crystallizes originating from the synthesis upon deprotonation of the salicylaldehyde reagent. It should also be noted that two molecules of co-crystallized HNEt<sub>3</sub>NO<sub>3</sub> are found in the unit cell (not shown in Figure 2) with the nitrate anions coming from the Yb reagent. The structural dependence of these Yb complexes on the substitution pattern (size of the 3-positioned group) of the aldehyde reagent and the incorporation of one or two salen ligands could lead to different reactivity and polymerization initiation properties. The influence of the aldehyde reagent on the structural properties and/or aggregation of oxophilic Zn(II)<sup>21</sup> and Mg(II)<sup>22</sup> centered salen complexes has also been described previously.

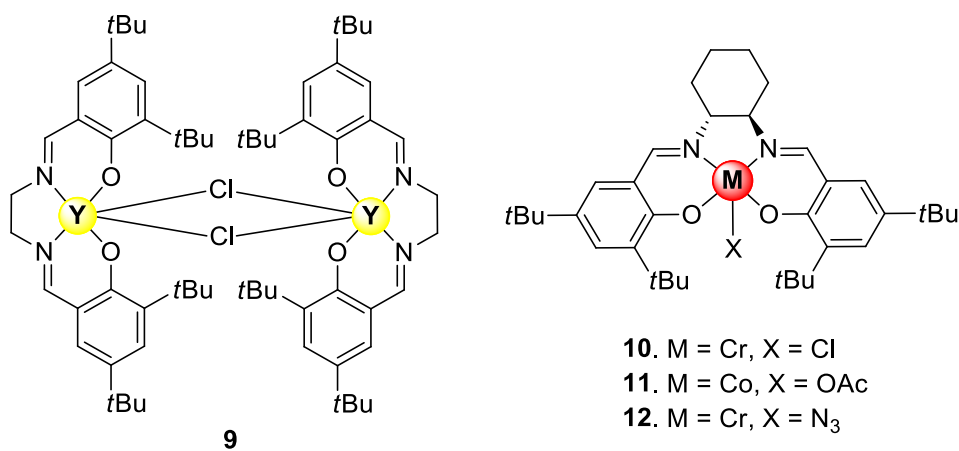


Beside the use of X-ray crystallography, mass analysis proved to be rather useful for identifying the molecular compositions of complexes **1-4** (see Supporting Information). In all cases either single isotope patterns for the complete structures (after loss of the neutral MeOH ligand) could be identified and/or major peaks related to the molecular ions having the MeOH ligand exchanged/replaced by H<sub>2</sub>O molecules. For complex **4** the intact anionic part of the molecular structure was easily identified and only the loss of the associated cation (HNEt<sub>3</sub><sup>+</sup>) could be observed. Complexes **1-4** were also further analyzed by UV-Vis and IR spectroscopy, <sup>1</sup>H paramagnetic NMR, and exact mass/elemental analyses (see also Supporting Information). The hemi-labile, bidentate *ortho*-formyl phenolate ligands in complexes **1-3** derived from the salicylaldehyde reagent likely prevents these complexes of forming multinuclear assemblies through bridging ligands. The phenolate moiety could potentially act as an initiator group during the catalytic copolymerization of epoxides and carbon dioxide, with the growing polymer chain formally displacing this anionic ligand after initiation.

Complexes **5** and **6**, based on scandium and yttrium, respectively, were synthesized following the extended silylamide route developed by Anwender and coworkers,<sup>16</sup> while complexes **7** and **8** were prepared conveniently from precursors **5** and **6**, respectively, by treatment with dry cyclohexanol (Scheme 2). The formation of complexes **7** and **8** was inferred from their <sup>1</sup>H NMR spectra; **5** and **6** both show a septuplet at 4.82 and 4.96 ppm, respectively, which disappeared upon reaction with cyclohexanol. Furthermore, the appearance of a broad singlet (CH–O–Ln unit) at 3.71 ppm and 4.17, respectively, is indicative of coordination of the cyclohexanolate ligand to the metal center.



**Scheme 2.** Synthesis of complexes **7** and **8** from known precursors **5** and **6** by ligand exchange.

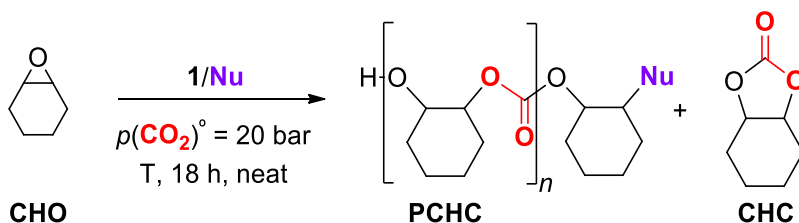


**Figure 3.** Benchmark complexes **9-12** for comparison with Yb complexes **1-4** in the catalytic copolymerization of CHO and CO<sub>2</sub>.

Finally, the dinuclear yttrium complex **9** (Figure 3) was prepared according to a procedure reported by Evans and coworkers,<sup>17</sup> whereas the metallosalen complexes **10-12** (M = Co or Cr; used as benchmark catalysts in the copolymerization studies, *vide infra*) were prepared according to procedures published by Jacobsen and coworkers.<sup>18</sup>

**Copolymerization studies with Yb-complex (1) :** For our initial experiments, cyclohexene oxide (CHO) was chosen as a benchmark substrate, and Yb-complex **1** was first tested as a potential catalyst for poly(cyclohexene)carbonate (PCHC) formation using an initial CO<sub>2</sub> pressure of 20 bar, a variety of co-catalysts and DCM as solvent (Table 2, entries 1–4). However, in these experiments only the formation of the corresponding cyclic carbonate product (CHC) was observed with generally low to moderate CHO conversion levels. The *cis*-configuration of the cyclic carbonate product CHC indicates the occurrence of a double inversion pathway (two separate S<sub>N</sub>2 type substitution reactions at the same carbon center),<sup>23</sup> and thus the CHC product does not likely originate from a typical backbiting process in a pre-formed polycarbonate leading to *trans*-CHC (cf., entry 9). When performing the copolymerization reaction under solvent-free conditions using Yb complex **1** as catalyst and lowering both the catalyst and nucleophile concentration ten-fold (entries 6–10), the carbonate selectivity switched dramatically and virtually only PCHC formation was observed with generally low polydispersity indices. It should be noted that in the absence of a co-catalytic additive (entry 5) no conversion could be observed suggesting that the complex **1** itself cannot initiate the copolymerization reaction under these conditions.<sup>24</sup> The use of five different co-catalysts was probed (entries 6–10) at 70°C, and the PCHC properties were compared. Whereas the use of DMAP, PPNBr and PPNI give copolymers of good quality (≥98% carbonate linkages), the molecular weight ( $M_n$ ) values only reach about 7.2 Kg/mol. As may be expected, the poorer leaving group ability of chloride allows for higher molecular weight polymers to be formed (entries 9 and 10), with an appreciable 11.4 Kg/mol when NBu<sub>4</sub>Cl is used. Although under these conditions the use of NBu<sub>4</sub>Cl gives higher molecular weight material, the presence of PPNCI allows for significantly higher conversion levels (22 versus 50%).

**Table 2.** Screening phase of the copolymerization between CHO and CO<sub>2</sub> using Yb-complex **1** as catalyst and various nucleophilic additives (co-cat). N.a. refers to not applicable and Nu is the nucleophilic additive used.<sup>a</sup>



Entry	<b>1</b> [mol%] <sup>b</sup>	Nu [mol%]	T [°C]	Conv. [%] <sup>c</sup>	TON <sup>d</sup>	TOF <sup>e</sup>	%CHC <sup>c</sup>	%PCHC <sup>c,f</sup>	M <sub>n</sub> <sup>g,h</sup> (M <sub>w</sub> /M <sub>n</sub> ) <sup>g</sup>
1	1.0	DMAP (1.0)	80	2 <sup>i</sup>	2	<1	>99 ( <i>cis</i> )	0	n.a.
2	1.0	PPNBr (1.0)	80	14 <sup>i</sup>	14	<1	>99 ( <i>cis</i> )	0	n.a.
3	1.0	PPNI (1.0)	100	48 <sup>i</sup>	47	3	>99 ( <i>cis</i> )	0	n.a.
4	1.0	PPNI (1.0)	70	46 <sup>i</sup>	45	3	>99 ( <i>cis</i> )	0	n.a.
5	0.1	–	70	0	0	0	trace	0	n.a.
6	0.1	DMAP (0.1)	70	36	356	20	1 ( <i>trans</i> )	98 (98)	3.70 (1.25)
7	0.1	PPNBr (0.1)	70	45	445	25	2 ( <i>trans</i> )	98 (99)	4.80 (1.42)
8	0.1	PPNI (0.1)	70	47	465	26	1 ( <i>trans</i> )	99 (99)	7.20 (1.53)
9	0.1	PPNCl (0.1)	70	50	494	27	2 ( <i>trans</i> )	98 (99)	9.10 (1.66)
10	0.1	NBu <sub>4</sub> Cl (0.1)	70	22	217	12	0	99 (99)	11.4 (1.35)

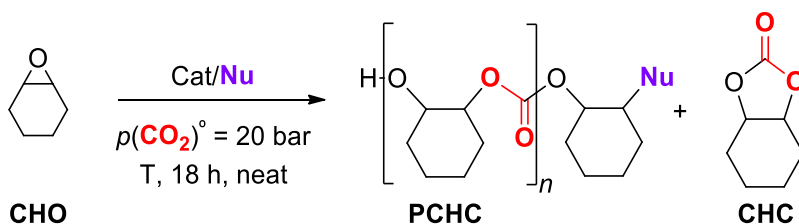
<sup>a</sup> Reactions were carried out in a 25 mL autoclave in neat cyclohexene oxide (CHO; 20 mmol), t = 18 h, p(CO<sub>2</sub>)<sup>o</sup> = 20 bar, DCM as solvent (5 mL; only entries 1-4). <sup>b</sup> Mol% of metal. <sup>c</sup> From the normalized integrals in the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of the methine resonances, including PCHC

( $\delta$ : 4.65 ppm), CHC [ $\delta$ : 3.90–4.00 ppm (*trans*) and 4.63 ppm (*cis*)], and the ether signal in impure PCHC ( $\delta$ : 3.45 ppm). <sup>d</sup> TON = (mol epoxide converted)/(mol catalyst). <sup>e</sup> TOF = TON/h. <sup>f</sup> In brackets the % of carbonate linkages; remaining % are ether linkages. <sup>g</sup> Determined by GPC analysis. <sup>h</sup> In Kg·mol<sup>-1</sup>. <sup>i</sup> Numbers refer to isolated yield.

**Comparative catalysis studies with Yb-complex (1) and Ln-salen complexes 5–9:** Next, we investigated the catalytic properties of known lanthanide salen complexes **5–9** and compared the activity and selectivity features of these reactions with those obtained with Yb-complex **1** in the copolymerization of CHO and CO<sub>2</sub> (Table 3). As observed for Yb complex **1**, for lanthanide complexes **5–9** the use of a chloride based initiator (nucleophile) also proved to be vital to access PCHC specifically at temperatures lower than 80°C. When scandium complex **5** was probed, both the use of PPnCl and PPNOAc initiators gave PCHC polymers of up to 4.5 Kg/mol with narrow polydispersities (1.4–1.6; entries 5 and 6). Upon exchange of the silylamide ligand in **5** for a cyclohexanolate (*i.e.*, Sc complex **6**) and combining with PPnX (X = Cl, N<sub>3</sub> or OAc; entries 7–10), the copolymerization reaction gave access to PCHC of higher molecular weight but at the expense of the chemoselectivity which was lower than observed for Yb complex **1** (*cf.*, entries 1 and 2). For the yttrium complex **7** the use of NBu<sub>4</sub>Cl fully reversed the chemoselectivity in favor of CHC (*cf.*, entry 12). The presence of PPnCl (entry 11), compared with the results obtained with Yb complex **1** (entry 1), gave a polymer of an appreciable molecular weight (10.5 Kg/mol) but with poorer control (PDI = 6.21). The increase in initial CO<sub>2</sub> pressure to 35 bar (entry 13) did not improve on this result showing similar polymer properties. When the silylamide ligand in **6** was replaced by a cyclohexanolate one (complex **8**), even poorer control over the PHCH quality was noted. Finally, bis-yttrium complex **9** was also subjected under the conditions reported for Yb complex **1** (entries 1 and 2) and again a PCHC polymer with a

reasonable molecular weight could be produced when PPNCI was present as initiator though the isolated polymer was poorly defined (PDI = 5.77). As had been

**Table 3.** Comparative studies for the copolymerization of CHO and CO<sub>2</sub> using Yb-complex **1** and lanthanide based catalysts **5–9**. N.a. refers to not applicable and Nu is the nucleophilic additive.<sup>a</sup>



Entry	Cat. [mol%] <sup>b</sup>	Nu [mol%]	T [°C]	Conv. [%] <sup>c</sup>	TON <sup>d</sup>	TOF <sup>e</sup>	%CHC <sup>c</sup>	%PCHC <sup>c,f</sup>	M <sub>n</sub> <sup>g,h</sup> (M <sub>w</sub> /M <sub>n</sub> ) <sup>g</sup>
1	<b>1</b> (0.1)	PPNCl (0.1)	70	50	494	27	2 ( <i>trans</i> )	98 (99)	9.10 (1.66)
2	<b>1</b> (0.1)	NBu <sub>4</sub> Cl (0.1)	70	22	217	12	0	99 (99)	11.4 (1.35)
3	<b>5</b> (0.1)	PPNBr (0.1)	100	75	741	41	99 (87% <i>cis</i> )	0	n.a.
4	<b>5</b> (0.1)	PPNCl (0.1)	100	70	692	38	99 (88% <i>cis</i> )	0	n.a.
5	<b>5</b> (0.1)	PPNCl (0.1)	70	64	640	36	5 ( <i>trans</i> )	95 (99)	4.00 (1.62)
6	<b>5</b> (0.1)	PPNOAc (0.1)	70	31	306	17	2 ( <i>trans</i> )	98 (99)	4.50 (1.46)
7	<b>6</b> (0.1)	PPNCl (0.1)	70	72	711	39	12 ( <i>trans</i> )	85 (99)	5.40 (1.91)
8	<b>6</b> (0.1)	PPNCl (0.05)	70	53	523	29	11 ( <i>trans</i> )	89 (99)	7.00 (1.41)
9	<b>6</b> (0.1)	PPNN <sub>3</sub> (0.1)	70	65	642	36	8 ( <i>trans</i> )	92 (99)	4.40

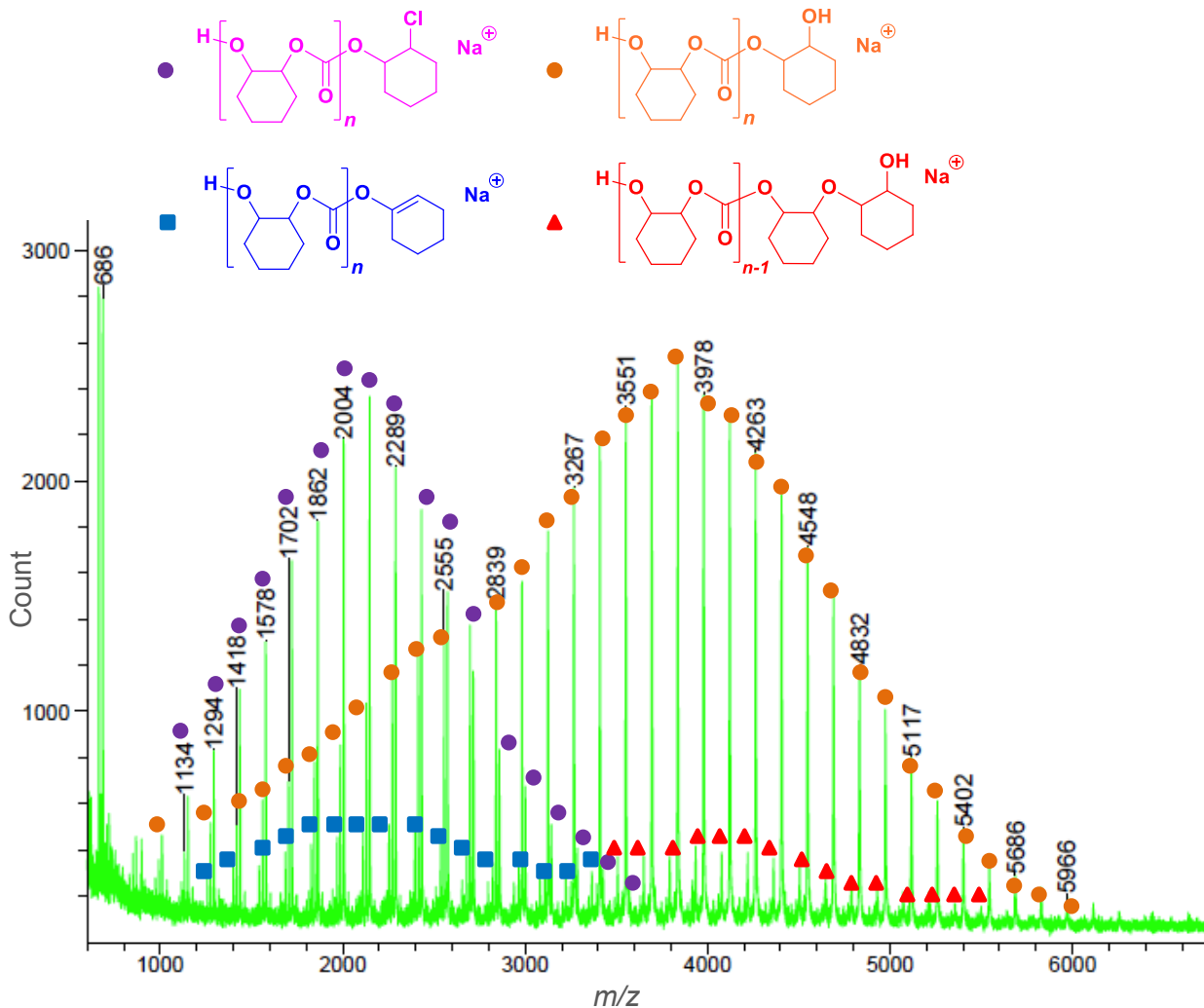
Entry	Cat. [mol%] <sup>b</sup>	Nu [mol%]	T [°C]	Conv. [%] <sup>c</sup>	TON <sup>d</sup>	TOF <sup>e</sup>	%CHC <sup>c</sup>	%PCHC <sup>c,f</sup>	M <sub>n</sub> <sup>g,h</sup> (M <sub>w</sub> /M <sub>n</sub> ) <sup>g</sup>
									(1.58)
10	<b>6</b> (0.1)	PPNOAc (0.1)	70	61	602	34	8 ( <i>trans</i> )	92 (99)	7.80 (1.57)
11	<b>7</b> (0.1)	PPNCl (0.1)	70	27	266	15	1 ( <i>trans</i> )	99 (99)	10.5 (6.21)
12	<b>7</b> (0.1)	NBu <sub>4</sub> Cl (0.1)	70	23	227	13	>99 (98% <i>cis</i> )	0	n.a.
13	<b>7</b> (0.1) <sup>i</sup>	PPNCl (0.1)	70	25	247	14	3 ( <i>trans</i> )	97 (99)	10.0 (7.83)
14	<b>8</b> (0.1)	PPNCl (0.05)	70	30	297	16	trace	99 (99)	10.4 (15.8)
15	<b>9</b> (0.1)	PPNCl (0.1)	70	9	89	5	4 ( <i>trans</i> )	96 (85)	9.00 (5.77)
16	<b>9</b> (0.1)	NBu <sub>4</sub> Cl (0.1)	70	12	119	7	>99 (97% <i>cis</i> )	0	n.a.

<sup>a</sup> Reactions were carried out in a 25 mL autoclave in neat cyclohexene oxide (CHO; 20 mmol), t = 18 h, p(CO<sub>2</sub>)<sup>o</sup> = 20 bar, neat. <sup>b</sup> Mol% of metal. <sup>c</sup> From the normalized integrals in the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of the methine resonances, including PCHC (δ: 4.65 ppm), CHC [δ: 3.90–4.00 ppm (*trans*) and 4.63 ppm (*cis*)], and the ether signal in impure PCHC (δ: 3.45 ppm). <sup>d</sup> TON = (mol epoxide converted)/(mol catalyst). <sup>e</sup> TOF = TON/h. <sup>f</sup> In brackets the % of carbonate linkages; remaining % are ether linkages. <sup>g</sup> Determined by GPC analysis. <sup>h</sup> In Kg·mol<sup>-1</sup>. <sup>i</sup> Initial CO<sub>2</sub> pressure was 35 bar.

noted for yttrium complex **7**, the combination of NBu<sub>4</sub>Cl with complex **9** led only to the formation of the cyclic carbonate product (entry 16). Comparatively, Yb complex **1** shows somewhat lower reactivity in relation to **5–9** but with much better copolymerization control combining high molecular weight, narrow polydispersities and very little formation of the CHC



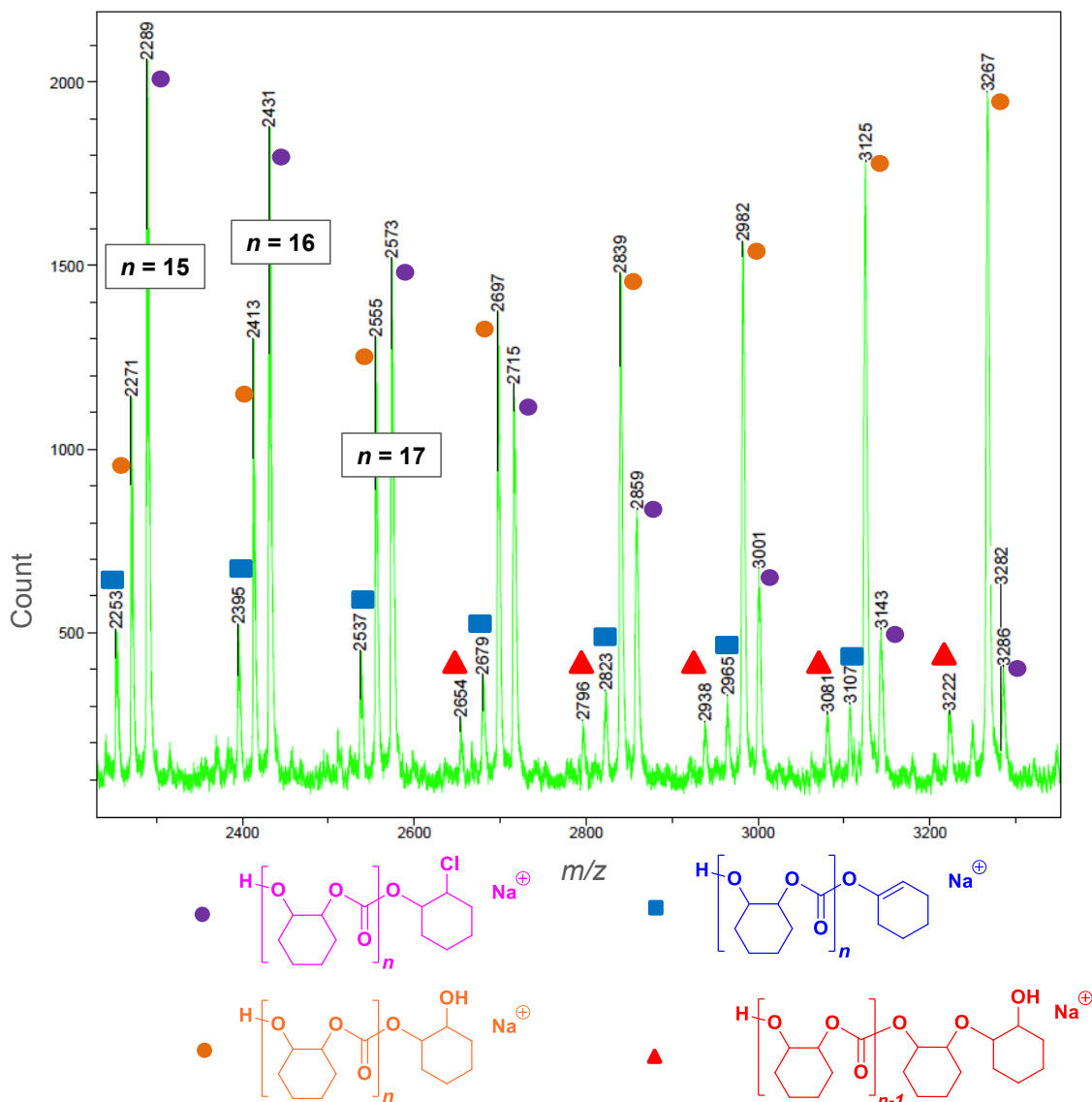
by-product. Comparison with other rare-earth metal based catalysts in the literature shows that Yb-complex **1** shows a combination of appreciable activity and good polymer selectivity in the coupling of CO<sub>2</sub> and CHO. For instance, Hou *et. al* reported on lanthanide complexes containing cyclopentadienyl ligands having high activity towards the synthesis of high molecular weight polycarbonates (13.7–25.6 Kg/mol) without using a co-catalytic additive. However, these catalysts typically exhibited lower (average) TOF values (between 3.7–9.4 h<sup>-1</sup>) than the ones reported here for complex **1**, and also gave rise to polycarbonates with higher polydispersities between 1.65–6.15.<sup>11b</sup>



**Figure 4.** MALDI-ToF spectrum of the PCHC product from Table 3 (entry 5) using scandium complex **5** as catalyst and PPNCI as initiator. Sampling conditions: dithranol matrix, NaOAc as additive in  $\text{CH}_2\text{Cl}_2/\text{THF}/\text{MeOH}$ .

In order to assess the properties of the produced PCHC in more detail, MALDI-TOF mass spectrometric analysis was performed on some representative samples (Figures 4 and 5, see also the Supporting Information for other examples)<sup>25</sup> which allowed for end-group analysis. In several cases where lower molecular weight polymers were formed we found evidence for chain-

transfer effects. Typically, the MALDI spectra recorded for these samples included isotopic distributions of polymers with different end-groups such as Cl, OH and cyclohexene (see inserts Figures 4 and 5). The latter two are indicative for 1,2-cyclohexanediol (CHD) acting as a chain transfer agent (CTA) of the growing polycarbonate as previously reported by Williams *et al.*<sup>25a</sup>



**Figure 5.** Expansion of the MALDI-ToF spectrum reported in Figure 4 (region  $m/z$  2200-3300). Some of the repeating units and the corresponding assigned peaks have been added.

As a result, two propagating species are present with one growing from Cl-induced polymer initiation whereas the other relates to CHD initiation (after chain transfer) that can propagate from both ends. This typically leads to the observation of bimodal distributions in the GPC analyses and this was indeed confirmed in most of the cases studied (Supporting Information for more details). Thus, it seems that traces of water or the presence of (traces of) CHD may be held responsible for the observation of some limitations of the polymer properties reported in Tables 2 and 3, and particularly the PCHC molecular weight. Most PCHC polymers produced were in fact found to have at least 98 % carbonate linkage content. The tacticity of the polymers was also determined using  $^{13}\text{C}$  NMR and showed the presence of syndiotactic (153.1 – 153.3 ppm) as well as isotactic (153.7 ppm) diads,<sup>26</sup> with the polymers thus being atactic (Supporting Information).

In order to assess whether further improvement of the PCHC properties could be realized, the copolymerization of CHO and  $\text{CO}_2$  was probed with the other Yb(salen) complexes **2–4** and the results compared with those obtained with Yb complex **1** (Table 4, entries 1 and 2). Structurally related Yb(salen) complexes **2** and **3** incorporating a cyclohexyl and a 1,2-diphenyl-ethylene bridging unit, respectively, showed inferior activities and polymer properties (lower  $M_n$ 's, and for **3** a much higher PDI; entries 3-5). This seems to indicate that the more rigid nature of the phenyl bridging group in Yb complex **1** positively influences the control over the copolymerization process. For Yb-*bis*-salen complex **4** we found that relative high molecular weight material may be accessed (about 15 Kg/mol) using either PPNBr or PPNI as initiator, however under these conditions the copolymerization control was extremely poor (entries 8 and 9). Slightly improved control over the polydispersity of the produced PCHC was noted when PPNCl was used as initiator (entry 6) but in this case the molecular weight was significantly

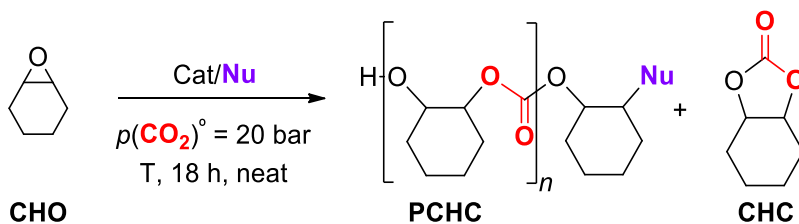
reduced (3919). The much higher PDI values reported for Yb-*bis*-salen complex **4** may be a result of various propagating species present after initiation by the nucleophilic additive, and complexes based on mono- or bis-Ln salen derivatives with more than one salen unit present do not seem to provide a good starting point for the development of highly active *and* selective copolymerization catalysts (cf., complex **9** Table 3). In complexes **1-3** the presence of a bidentate phenolate ligand derived from the salicylaldehyde reagent leads to more defined catalyst species after initiation. In the case of **4**, lacking such a ligand, multiple active catalytic species may be responsible for the lower quality of polycarbonate formed under comparatively similar reaction conditions reported for catalysts based on **1-3**.

Finally, to benchmark the catalysis features of our best-performing catalyst **1**, we tested known catalysts **10-12** reported by the groups of Darensbourg and Coates (Table 5).<sup>27,28</sup> Both the activity and selectivity profiles for Yb salen complex **1** were evaluated against those obtained for Cr(III) and Co(III) salen complexes **10-12** under similar experimental conditions and using the same reactor set up. Complexes **10-12** are well-known copolymerization catalysts for the CHO/CO<sub>2</sub> coupling reaction typically giving rise to PCHC having molecular weights of up to 30 Kg/mol and initial high reactivity with TOFs in the range 250–450 h<sup>-1</sup> using polymerization initiators of type PPN-X (X = Cl, N<sub>3</sub>, OAc).<sup>27,28</sup>

The activities and selectivity profiles of the Cr and Co salen catalysts **10-12** (Table 5, entries 8-11) were determined under comparable reaction conditions (cf., entries 1 and 2) and our reactor system generally gave PCHC products of somewhat higher molecular weight ( $M_n$ 's between 13.2–13.7 Kg/mol, PDI's 1.3–1.7) than the polymers obtained by using Yb salen complex **1** without too much difference between the three systems. These results show that under the applied copolymerization conditions (i.e., the best ones for Yb complex **1**) there is no

significant influence of the metal ion (Cr versus Co) and axial ligand (Cl versus OAc versus N<sub>3</sub>) bound to the metal center. The average TOF values reported for the complexes **10–12** were also higher (36–44 h<sup>-1</sup>) than noted for **1** (entry 1; 27 h<sup>-1</sup>). Better reactivity for **1** could be realized by

**Table 4.** Comparative studies for the copolymerization of CHO and CO<sub>2</sub> using Yb-complexes **1-4**. N.a. refers to not applicable and Nu stands for nucleophilic additive.<sup>a</sup>



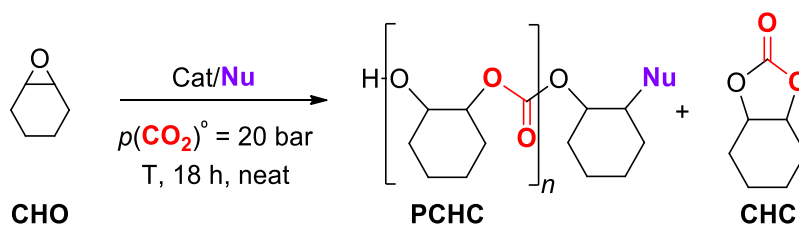
Entry	Cat.	Nu	T	Conv.	TON <sup>d</sup>	TOF <sup>e</sup>	%CHC <sup>c</sup>	%PCHC <sup>c,f</sup>	M <sub>n</sub> <sup>g,h</sup>
	[mol%] <sup>b</sup>	[mol%]	[°C]	[%] <sup>c</sup>					(M <sub>w</sub> /M <sub>n</sub> ) <sup>g</sup>
1	<b>1</b> (0.1)	PPNCl (0.1)	70	50	494	27	2 ( <i>trans</i> )	98 (99)	9.10 (1.66)
2	<b>1</b> (0.1)	NBu <sub>4</sub> Cl (0.1)	70	22	217	12	0	99 (99)	11.4 (1.35)
3	<b>2</b> (0.1)	PPNCl (0.1)	70	34	340	14	99 ( <i>cis</i> )	traces	n.a.
4	<b>2</b> (0.1)	PPNCl (0.05)	70	22	217	12	1 ( <i>trans</i> )	99 (99)	4.60 (1.26)
5	<b>3</b> (0.1)	PPNCl (0.1)	70	34	336	19	3 ( <i>trans</i> )	97 (99)	6.10 (5.12)
6	<b>4</b> (0.1)	PPNCl (0.1)	70	39	385	21	4 ( <i>trans</i> )	96 (99)	4.00 (10.1)
7	<b>4</b> (0.1)	NBu <sub>4</sub> Cl (0.1)	70	32	316	18	5 ( <i>trans</i> )	95 (99)	9.00 (19.5)
8	<b>4</b> (0.1)	PPNBr (0.1)	70	35	346	19	2 ( <i>trans</i> )	98 (98)	15.1 (12.1)
9	<b>4</b> (0.1)	PPNI (0.1)	70	55	544	30	5 ( <i>trans</i> )	95 (99)	15.3 (14.0)

<sup>a</sup> Reactions were carried out in a 25 mL autoclave in neat cyclohexene oxide (CHO; 20 mmol), t = 18 h, p(CO<sub>2</sub>)<sup>o</sup> = 20 bar, neat. <sup>b</sup> Mol% of metal. <sup>c</sup> From the normalized integrals in the <sup>1</sup>H NMR

spectra ( $\text{CDCl}_3$ ) of the methine resonances, including PCHC ( $\delta$ : 4.65 ppm), CHC [ $\delta$ : 3.90–4.00 ppm (*trans*) and 4.63 ppm (*cis*)], and the ether signal in impure PCHC ( $\delta$ : 3.45 ppm). <sup>d</sup> TON = (mol epoxide converted)/(mol catalyst). <sup>e</sup> TOF = TON/h. <sup>f</sup> In brackets the % of carbonate linkages; remaining % ether linkages. <sup>g</sup> Determined by GPC analysis. <sup>h</sup> In  $\text{Kg}\cdot\text{mol}^{-1}$ .



**Table 5.** Comparative studies for the copolymerization of CHO and CO<sub>2</sub> using Yb-complex **1** and Co/Cr-salen complexes **10-12**. N.a. refers to not applicable and Nu stands for nucleophilic additive.<sup>a</sup>



Entry	Cat. [mol%] <sup>b</sup>	Nu [mol%]	T [°C]	Conv. [%] <sup>c</sup>	TON <sup>d</sup>	TOF <sup>e</sup>	%CHC <sup>c</sup>	%PCHC <sup>c,f</sup>	M <sub>n</sub> <sup>g,h</sup> (M <sub>w</sub> /M <sub>n</sub> ) <sup>g</sup>
1	<b>1</b> (0.1)	PPNCl (0.1)	70	50	494	27	2 ( <i>trans</i> )	98 (99)	9.10 (1.66)
2	<b>1</b> (0.1)	NBu <sub>4</sub> Cl (0.1)	70	22	217	12	0	99 (99)	11.4 (1.35)
3	<b>1</b> (0.01)	PPNCl (0.01)	70	10	1000	55	99 ( <i>cis</i> )	traces	n.a.
4	<b>1</b> (0.05)	NBu <sub>4</sub> Cl (0.05)	70	40	800	44	2 ( <i>trans</i> )	98 (99)	3.00 (1.78)
5	<b>1</b> (0.1)	NBu <sub>4</sub> Cl (0.05)	70	13	128	7	traces	99 (99)	3.40 (1.26)
6	<b>1</b> (0.1)	NBu <sub>4</sub> Cl (0.05)	90	57	563	31	traces	99 (99)	10.2 (1.54)
7	<b>1</b> (0.01)	PPNCl (0.01)	90	15	1500	83	4 ( <i>trans</i> )	96 (99)	4.60 (5.37)
8	<b>10</b> (0.1)	PPNCl (0.1)	70	75	741	41	7 ( <i>trans</i> )	93 (99)	13.2 (1.69)
9	<b>11</b> (0.1)	PPNCl (0.1)	70	81	801	44	1 ( <i>trans</i> )	98 (99)	13.6 (1.33)

Entry	Cat. [mol%] <sup>b</sup>	Nu [mol%]	T [°C]	Conv. [%] <sup>c</sup>	TON <sup>d</sup>	TOF <sup>e</sup>	%CHC <sup>c</sup>	%PCHC <sup>c,f</sup>	M <sub>n</sub> <sup>g,h</sup> (M <sub>w</sub> /M <sub>n</sub> ) <sup>g</sup>
10	<b>12</b> (0.1)	PPNCl (0.1)	70	74	731	41	traces	99 (99)	13.7 (1.87)
11	<b>12</b> (0.1)	PPNN <sub>3</sub> (0.1)	70	66	652	36	1 ( <i>trans</i> )	99 (99)	13.1 (1.59)
12	<b>1</b> (0.1)	PPNN <sub>3</sub> (0.1)	70	55	544	30	1 ( <i>trans</i> )	99 (99)	6.50 (1.35)
13	<b>1</b> (0.1)	PPNOAc (0.1)	70	68	672	37	3 ( <i>trans</i> )	97 (99)	7.50 (1.57)

<sup>a</sup> Reactions were carried out in a 25 mL autoclave in neat cyclohexene oxide (CHO; 20 mmol), t = 18 h, p(CO<sub>2</sub>)<sup>o</sup> = 20 bar, neat. <sup>b</sup> Mol% of metal. <sup>c</sup> From the normalized integrals in the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of the methine resonances, including PCHC ( $\delta$ : 4.65 ppm), CHC [ $\delta$ : 3.90–4.00 ppm (*trans*) and 4.63 ppm (*cis*)], and the ether signal in impure PCHC ( $\delta$ : 3.45 ppm). <sup>d</sup> TON = (mol epoxide converted)/(mol catalyst). <sup>e</sup> TOF = TON/h. <sup>f</sup> In brackets the % of carbonate linkages; remaining % are ether linkages. <sup>g</sup> Determined by GPC analysis. <sup>h</sup> In Kg·mol<sup>-1</sup>.

variation of the co-catalytic additive and the type of anion (entries 4, 6, 7, 12 and 13) but in each case at the expense of the molecular weight of the isolated PCHC. The best compromise between reactivity and polymer weight is the use of Yb complex **1** with NBu<sub>4</sub>Cl as initiator at 90°C giving a TOF value of 31 h<sup>-1</sup> and an M<sub>n</sub> of 10.2 Kg/mol (PDI = 1.54). The benchmark studies carried out for **1** and comparing its reactivity and selectivity features with those of **10–12** in the copolymerization of CHO and CO<sub>2</sub> demonstrate clearly that the Yb salen complex **1** has good reactivity and allows for the highly selective formation of PCHC of excellent quality unlike the other lanthanide based systems reported in this work.

## CONCLUSION

We here describe the synthesis of discrete mononuclear Yb complexes based on salen ligands and their full characterization. These complexes have been used as (pre)catalysts for the copolymerization reaction of CHO and CO<sub>2</sub> to afford polycarbonates,<sup>29</sup> and their reactivity and selectivity profiles, in particular for complex **1**, have been benchmarked using the measured profiles of a series of known lanthanide salen complexes, and the well-known Cr(III)- and Co(III)salen catalysts. Whereas the reactivity and selectivity features of **1** are clearly much more attractive than observed for the other lanthanide complexes **5-9**, lower reactivity (TOFs) and somewhat lower M<sub>n</sub> values were achieved when evaluating against the Co and Cr(salen) based catalyst systems using similar reaction conditions in the same reactor set up. Nonetheless, Yb complex **1** reports high quality PCHC product of appreciable molecular weight (10–11 Kg/mol) under mild conditions (70°C, 0.1 mol% cat/PPNCl, *p*(CO<sub>2</sub>) = 20 bar) and further optimization of the reactivity of such Yb based catalysts derived from other types of aminophenolate ligands should be feasible, including the design of binary and bifunctional type catalysts.

## ASSOCIATED CONTENT

**Supporting Information.** Copies of analytical data for complexes **1-4**, spectra of isolated PCHC polymer samples, representative MALDI-ToF and corresponding GPC traces, and cif files for the X-ray molecular structures reported for complexes **1** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

[akleij@iciq.es](mailto:akleij@iciq.es)

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We thank the Spanish MINECO (projects CTQ2011-27385 and CTQ-2014-60419-R) and support through Severo Ochoa Excellence Accreditation 2014-2018 (SEV-2013-0319), ICIQ, ICREA, and Sabic Ltd. for generous support to the results described herein. CM thanks the Marie Curie COFUND action from the European Commission for co-financing a postdoctoral fellowship. Dr. Noemí Cabello, Sofía Arnal, and Vanessa Martínez are acknowledged for the MALDI-ToF analyses, Dr. L. Jasinska for GPC measurements and Prof. Sandro Gambarotta, Dr. Rob Duchateau, Dr. Jason Morton, Dirk Beetstra, Dr. Atieh Abu Raqabah for valuable discussions concerning the copolymerization results.

## REFERENCES

- (1) (a) Aresta, M., Ed.; *Carbon Dioxide as Chemical Feedstock*; Wiley-VCH: New York, 2010. (b) Quadrelli, E. A.; Centi, G.; Duplan, J. L.; Perathoner, S. *ChemSusChem* **2011**, *4*, 1194-1215. (c) Aresta, M.; Dibenedetto, A.; Angelini, A. *Chem. Rev.* **2014**, *114*, 1709-1742. (d) Kielland, N.; Whiteoak, C. J.; Kleij, A. W. *Adv. Synth. Catal.* **2013**, *355*, 2115-2138. (e) Peters, M.; Köhler, B.; Kuckshinrichs, W.; Leitner, W.; Markewitz, P.; Müller, T. E. *ChemSusChem* **2011**, *4*, 1216-1240. (f) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem. Int. Ed.* **2011**, *50*, 8510-8537. (g) Maeda, H.; Miyazaki, Y.; Ema, T. *Catal. Sci. Technol.* **2014**, *4*, 1482-1497.
- (2) (a) Decortes, A.; Castilla, A. M.; Kleij, A. W. *Angew. Chem. Int. Ed.* **2010**, *49*, 9822-9837. (b) North, M.; Pasquale, R.; Young, C. *Green Chem.* **2010**, *12*, 1514-1539. (c) Pescarmona, P. P.; Taherimehr, M. *Catal. Sci. Technol.* **2012**, *2*, 2169-2187. (d) Comerford, J. W.; Ingram, I. D. V.; North, M.; Wu, X. *Green Chem.* **2015**, *17*, 1966-1987. (e) Fiorani, G.; Guo, W.; Kleij, A. W. *Green Chem.* **2015**, *17*, 1375-1389.
- (3) (a) Coates, G. W.; Moore, D. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 6618-6639. (b) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388-2410. (c) Kember, M. R.; Buchard, A.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 141-163. (d) Lu, X.-B.; Darensbourg, D. J. *Chem. Soc. Rev.* **2012**, *41*, 1462-1484. (e) Klaus, S.; Lehenmeier, M. W.; Anderson, C. E.; Rieger, B. *Coord. Chem. Rev.* **2011**, *255*, 1460-1479. (f) Lu, X.-B.; Ren, W.-M.; Wu, G.-P. *Acc. Chem. Res.* **2012**, *45*, 1721-1735. (g) Nozaki, K. *Pure Appl. Chem.* **2004**, *76*, 541-546. (h) Childers, M. I.; Longo, J. M.; Van Zee, N. J.; LaPointe, A. M.; Coates, G. W. *Chem. Rev.* **2014**, *114*, 8129-8152.

(4) For specific examples: (a) Cohen, C. T.; Chu, Y.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869–10878. (b) Wu, G.-P.; Wei, S.-H.; Ren, W.-M.; Lu, X.-B.; Xu, T.-Q.; Darensbourg, D. J. *J. Am. Chem. Soc.* **2011**, *133*, 15191-15199. (c) Darensbourg, D. J.; Wilson, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 18610-18613. (d) Wu, G.-P.; Xu, P.-X.; Lu, X.-B.; Zu, Y.-P.; Wei, S.-H.; Ren, W.-M.; Darensbourg, D. J. *Macromolecules* **2013**, *46*, 2128–2133. (e) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers J. L. *J. Am. Chem. Soc.* **2005**, *127*, 14026-14038. (f) Lu, X.-B.; Liang, B.; Zhang, Y.-J.; Tian, Y.-Z.; Wang, Y.-M.; Bai, C.-X.; Wang, H.; Zhang, R. *J. Am. Chem. Soc.* **2004**, *126*, 3732–3733. (g) Wu, G.-P.; Ren, W.-M.; Luo, Y.; Li, B.; Zhang, W.-Z.; Lu, X.-B. *J. Am. Chem. Soc.* **2012**, *134*, 5682–5688.

(5) (a) Darensbourg, D. J.; Billodeaux, D. R. *Inorg. Chem.* **2005**, *44*, 1433–1442; (b) Aida, T. and Inoue, S. *Macromolecules* **1982**, *15*, 682-684. (c) Chatterjee, C.; Chisholm, M. H. *Inorg. Chem.* **2011**, *50*, 4481–4492. For a review on Al-catalysis: (d) Ikpo, N.; Flogeras, J. C.; Kerton, F. M. *Dalton Trans.* **2013**, *42*, 8998-9006.

(6) (a) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. *Angew. Chem. Int. Ed.* **2009**, *48*, 931–933. (b) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404–11405. (c) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284–14285 (d) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008–11009. (e) Ellis, W. C.; Jung, Y.; Mulzer, M.; Di Girolamo, R.; Lobkovsky, E. B.; Coates, G. W. *Chem. Sci.* **2014**, *5*, 4004-4011. See also the ring-opening polymerization of cyclic carbonates: (f) del Rosal, I.; Brignou, P.; Guillaume, S. M.; Carpentier, J.-F.; Maron, L. *Polym. Chem.* **2011**, *2*, 2564-2573.

(7) Kember, M. R.; Williams, C. K. *J. Am. Chem. Soc.* **2012**, *134*, 15676–15679.

(8) (a) Buchard, A.; Kember, M. R.; Sandeman, K. G.; William, C. K. *Chem. Commun.* **2011**, 47, 212-214. (b) Taherimehr, M.; Al-Amsyar, S. M.; Whiteoak, C. J.; Kleij, A. W.; Pescarmona, P. P. *Green Chem.* **2013**, 15, 3083-3090.

(9) (a) Sugimoto, H., Ohshima, H. and Inoue, S. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, 41, 3549-3555. (b) Robert, C.; Ohkawara, T.; Nozaki, K. *Chem. Eur. J.* **2014**, 20, 4789-4795.

(10) (a) Vitanova, D. V.; Hampel, F.; Hultsch, K. C. *J. Organomet. Chem.* **2005**, 690, 5182–5197. (b) Lazarov, B. B.; Hampel, F.; Hultsch, K. C. *Z. Anorg. Allg. Chem.* **2007**, 633, 2367–2373.

(11) (a) Cui, D.; Nishiura, M.; Hou, Z. *Macromolecules* **2005**, 38, 4089–4095. (b) Cui, D.; Nishiura, M.; Tardif, O.; Hou, Z. *Organometallics* **2008**, 27, 2428–2435.

(12) Zhang, Z.; Cui, D.; Liu, X. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, 46, 6810–6818.

(13) (a) Bakewell, C.; Cao, T.-P.-A.; Long, N.; Le Goff, X. F.; Auffrant, A.; Williams, C. K. *J. Am. Chem. Soc.* **2012**, 134, 20577–20580. (b) Sinenkov, M. A.; Fukin, G. K.; Cherkasov, A. V.; Ajellal, N.; Roisnel, T.; Kerton, F. M.; Carpentier, J.-F.; Trifonov, A. A. *New J. Chem.* **2011**, 35, 204-212. (c) Brignou, P.; Priebe Gil, M.; Casagrande, O.; Carpentier, J.-F.; Guillaume, S. M. *Macromolecules*, **2010**, 43, 8007–8017. (d) Gu, W.; Xu, P.; Wang, Y.; Yao, Y.; Yuan, D.; Shen, Q. *Organometallics* **2015**, 34, 2907-2916. (e) Wang, C.; Liu, X.; Dai, Z.; Sun, Y.; Tang, N.; Wu, J. *Inorg. Chem. Commun.* **2015**, 56, 69-72. (f) Altenbuchner, P. T.; Kronast, A.; Kissling, S.; Vagin, S. I.; Herdtweck, E.; Pöthig, A.; Deglmann, P.; Loos, R.; Rieger, B. *Chem. Eur. J.* **2015**, DOI: 10.1002/chem.201501156. (g) Carpentier, J.-F. *Organometallics* **2015**, DOI: 10.1021/acs.organomet.5b00540.

- (14) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2008**, *47*, 11868–11878.
- (15) Kozitsyna, N. Y.; Bukharkina, A. A.; Martens, M. V.; Vargaftik M. N.; Moiseev, I. I. *J. Organomet. Chem.* **2001**, *636*, 69–75.
- (16) (a) Liu, Q.; Meermann, C.; Görlitzer, H. W.; Runte, O.; Herdtweck, E.; Sirsch, P.; Törnroos, K. W.; Anwander, R. *Dalton Trans.* **2008**, 6170–6178. (b) Meermann, C.; Törnroos, K. W.; Anwander, R. *Inorg. Chem.* **2009**, *48*, 2561–2570. (c) Runte, O.; Priermeier, T.; Anwander, R. *Chem. Commun.* **1996**, 1385–1386.
- (17) Evans, W. J.; Fujimoto, C. H.; Ziller, J. W. *Chem. Commun.* **1999**, 311–312.
- (18) Complex **12**: (a) Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5897–5898. Complex **13**: (b) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936–938. Complex **14**: (c) Leighton, J. L.; Jacobsen, E. N. *J. Org. Chem.* **1996**, *61*, 389–390.
- (19) Blessing, R. H. *Acta Cryst.* **1995**, *A51*, 33–38.
- (20) Sheldrick, G. M. SHELXL, version 6.14, Bruker-AXS, Madison (WI), USA, **2003**.
- (21) For detailed studies: (a) Elemans, J. A. A. W.; Wezenberg, S. J.; Escudero-Adán, E. C.; Benet-Buchholz, J.; den Boer, D.; Coenen, M. J. J.; Speller, S.; Kleij, A. W.; de Feyter, S. *Chem. Commun.* **2010**, *46*, 2548–2550. (b) Martínez Belmonte, M.; Wezenberg, S. J.; Haak, R. M.; Anselmo, D.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. W. *Dalton Trans.* **2010**, *39*, 4541–4550. (c) Salassa, G.; Coenen, M. J. J.; Wezenberg, S. J.; Hendriksen, B. L. M.; Speller, S.; Elemans, J. A. A. W.; Kleij, A. W. *J. Am. Chem. Soc.* **2012**, *134*, 7186–7192. (d) Escárcega-



Bobadilla, M. V.; Zelada-Guillén, G. A.; Pyrlin, S. V.; Wegrzyn, M.; Ramos, M. M. D.; Giménez, E.; Stewart, A.; Maier, G.; Kleij, A. W. *Nature Commun.* **2013**, *4*, 2648.

(22) Miyasaka, H.; Clérac, C.; Ishii, T.; Chang, H.-C.; Kitagawa, S.; Yamashita, M. *J. Chem. Soc. Dalton Trans.* **2002**, 1528–1534.

(23) See for a discussion on the “double inversion” pathway: (a) Langanke, J.; Greiner, L.; Leitner, W. *Green Chem.* **2013**, *15*, 1173–1182. (b) Darensbourg, D. J.; Wilson, S. J. *Green Chem.* **2012**, *14*, 2665–2671. (c) Whiteoak, C. J.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. *Adv. Synth. Catal.* **2013**, *355*, 2233–2239. (d) Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 212–214.

(24) Apparently, either the bidentate coordination nature of the formyl-phenolate ligand is preserved under these conditions and/or this phenolate anion is not nucleophilic enough.

(25) For exemplary contributions regarding MALDI-TOF analysis of polycarbonate polymers: (a) Jutz, F.; Buchard, A.; Kember, M. R.; Fredriksen, S. B.; Williams, C. K. *J. Am. Chem. Soc.* **2011**, *133*, 17395–17405. (b) Duchateau, R.; van Meerendonk, W. J.; Yajjou, L.; Staal, B. B. P.; Koning, C. E.; Gruter, G.-J. M. *Macromolecules* **2006**, *39*, 7900–7908.

(26) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans.* **2006**, 237–249.

(27) (a) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335–6342. (b) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem.* **2004**, *43*, 1831–1833. (c) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024–6034. See also reference 4e.

(28) Nakano, K.; Nozaki, K.; Hiyama, T. *Macromolecules* **2001**, *34*, 6325–6332.

(29) Preliminary attempts to copolymerize propylene oxide and CO<sub>2</sub> to afford polycarbonate have been unsuccessful as only cyclic carbonate formation was observed; see Table S1 in the Supporting Information for details.