

Supporting Information

Dinuclear Metal Catalysts: Improved Performance of Heterodinuclear Mixed Catalysts for CO₂/Epoxide Copolymerization

Prabhjot K. Saini, Charles Romain and Charlotte K. Williams

Department of Chemistry, Imperial College London, London, SW7 2AZ

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Experimental Section

Materials and Methods

The synthesis of H₂L was carried out as previously reported.¹ The synthesis of metal complexes **1**, **2**, and **3** were carried out under anhydrous conditions, using either a Schlenk line or a nitrogen-filled glovebox. Catalysts **1** and **2** were synthesised according to literature procedure.^{1,2}

All solvents and reagents were obtained from Sigma Aldrich and Strem. THF was dried by refluxing over sodium and benzophenone and stored under nitrogen. Cyclohexene oxide (CHO) was dried over MgSO₄ and fractionally distilled under nitrogen. All dry solvents and reagents were stored under nitrogen and degassed by several freeze-pump-thaw cycles. Research grade carbon dioxide was used for copolymerization studies. The high pressure copolymerization reactions were carried out in a Parr 5513 100 mL bench reactor.

¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AV-400 instrument, unless otherwise stated. All mass spectrometry measurements were performed using a MALDI micro MX micromass instrument. The matrix used was dithranol with KOAc as the ionising agent and THF as the solvent. Elemental Analysis was determined by Stephen Boyer at London Metropolitan University and Alan Dickerson at Cambridge University. Size exclusion chromatography was recorded by a Polymer labs PL GPC-50 instrument. THF was used as the eluent, at a flow rate of 1 mLmin⁻¹. Two polymer labs mixed D columns were used and calibration was carried out by using narrow M_w polystyrene standards.

Preparation of Catalyst System 3

H₂L (0.60 g, 1.09 mmols) was dissolved in dry THF (30 mL) and cooled to -20 °C. Et₂Zn (0.14 g, 1.09 mmols) was dissolved in dry THF (10 mL) and cooled to -20 °C. The Et₂Zn solution was added dropwise to the pro-ligand solution, at -20 °C and was allowed to warm, over 4 h, to 25 °C. Then, Mg(OAc)₂ (0.16 g, 1.09 mmols) was added to the reaction mixture and this was left to stir for 16 h. The solvent was removed under vacuum to produce a white solid (0.70 g, 85%). Calc. for C₃₈H₆₀O₂N₂MgZn : C, 60.17; H, 7.97; N, 7.39; Found: C, 59.88; H, 7.87; N, 7.31 %; MS (MALDI-TOF): m/z 697 ([LMgZn(OAc)]⁺, 100%), 657 ([LMg₂(OAc)]⁺, 25%), 739 ([LZn₂(OAc)]⁺, 45%); ¹³C NMR (400 MHz, C₆D₆): δC =176.2, 163.5, 135.6, 125.9, 123.6, 62.3, 56.2, 34.2, 32.1, 27.9, 26.5, 24.4, 20.9 ppm.

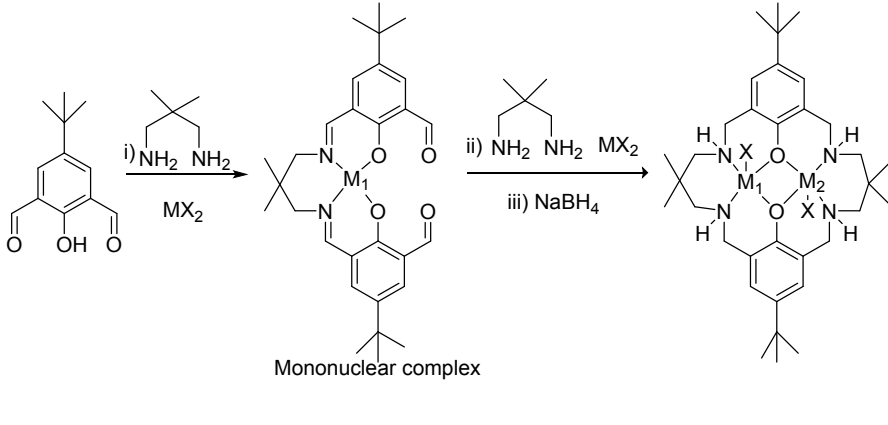
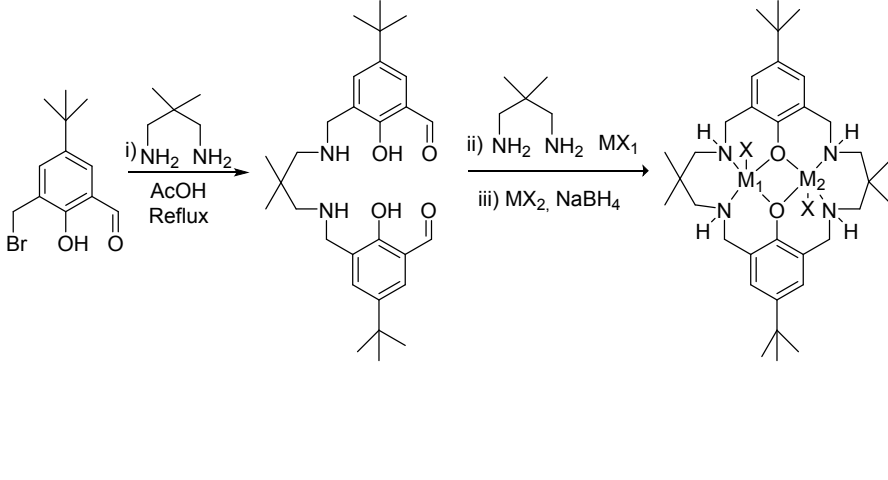
Low Pressure Copolymerization Reactions

Distilled and dried cyclohexene oxide (2.5 mmol, 25 mmol) and the catalyst (0.025 mmol) were placed in a Schlenk tube. The reaction mixture was de-gassed and then heated to 80 °C at 1 bar CO₂ pressure. After a certain reaction time, the mixture was quenched by exposure to air and a ¹H NMR spectrum of the crude mixture was recorded. Then, the cyclohexene oxide was removed, under vacuum, to yield the polycarbonate, which was purified by dissolving it in THF and precipitating it with MeOH.

High Pressure Copolymerization Reactions

The Parr reactor was dried for 20 h at 140 °C and purged with CO₂ three times and allowed to cool to 25 °C. Then, the catalyst (0.03 mmol) dissolved in cyclohexene oxide (15 mL, 148 mmol) was added to the Parr reactor. After sealing the reactor, 50 bar of CO₂ was added whilst the reaction mixture was stirring at a low-frequency in order to facilitate CO₂ dissolution. This step was repeated several times until the CO₂ dissolution reached equilibrium and the headspace pressure remained constant. The vessel was heated to the appropriate temperature and stirred for a certain time and then a ¹H NMR spectrum of the crude reaction mixture was recorded. The mixture was then taken up in methylene chloride and evaporated to dryness. The white powder polymer was purified by dissolving it in THF and then precipitation with MeOH.

Table S1: All other synthetic routes carried out to produce a heterodinuclear complex, which were unsuccessful.

Synthetic Route	Reagents and Conditions	Comments and Problems
 <p style="text-align: center;">Mononuclear complex</p>	<ol style="list-style-type: none"> 1. i) $\text{MX}_2 = \text{Zn}(\text{OAc})_2$, MeOH, Reflux 2. i) $\text{MX}_2 = \text{Cu}(\text{OAc})_2$, MeOH, 40 °C, ii) $\text{MX}_2 = \text{Zn}(\text{OAc})_2$, THF 40 °C. 3. i) $\text{MX}_2 = \text{MgNO}_3 \cdot 6\text{H}_2\text{O}$, MeOH, 60 °C 4. i) $\text{MX}_2 = \text{Zn}(\text{BF})_4$, MeOH, 40 °C 	<ol style="list-style-type: none"> 1. Yielded only 50% of complex 1 (i.e. $\text{LZn}_2(\text{OAc})_2$) 2. i) yielded the target mono-copper compound. ii) reaction failed, only mono-copper species isolated. 3. Low yield of target mono-magnesium complex, contaminated by polymeric by-products which were inseparable. 4. Formation of polymers only
		<p>The reaction was repeated several (>3) times leading only to complex mixtures, including substantial amounts of polymers.</p> <p>Attempts to protect the formyl functionality to improve the reaction selectivity were unsuccessful despite the use of different protecting groups (ortho-formates)</p>

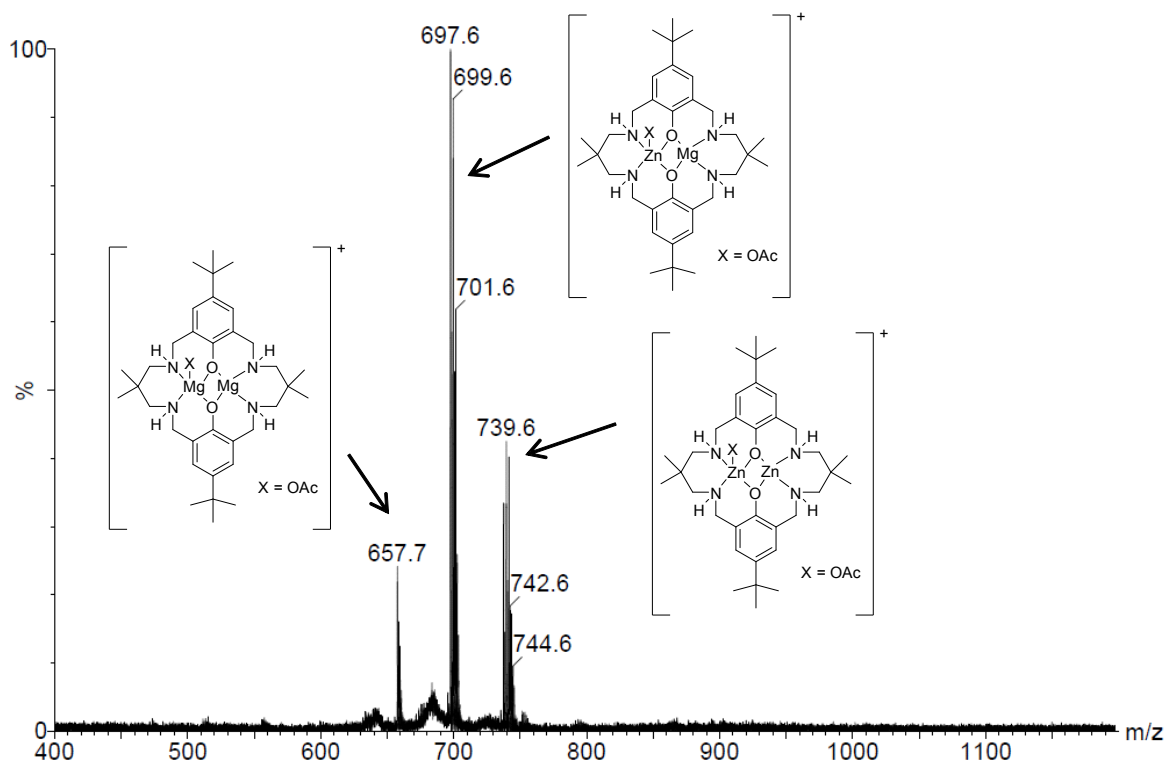


Figure S1: Full MALDI-ToF spectrum of catalyst system **3**, with the assignment of the signals due to the molecular ions.

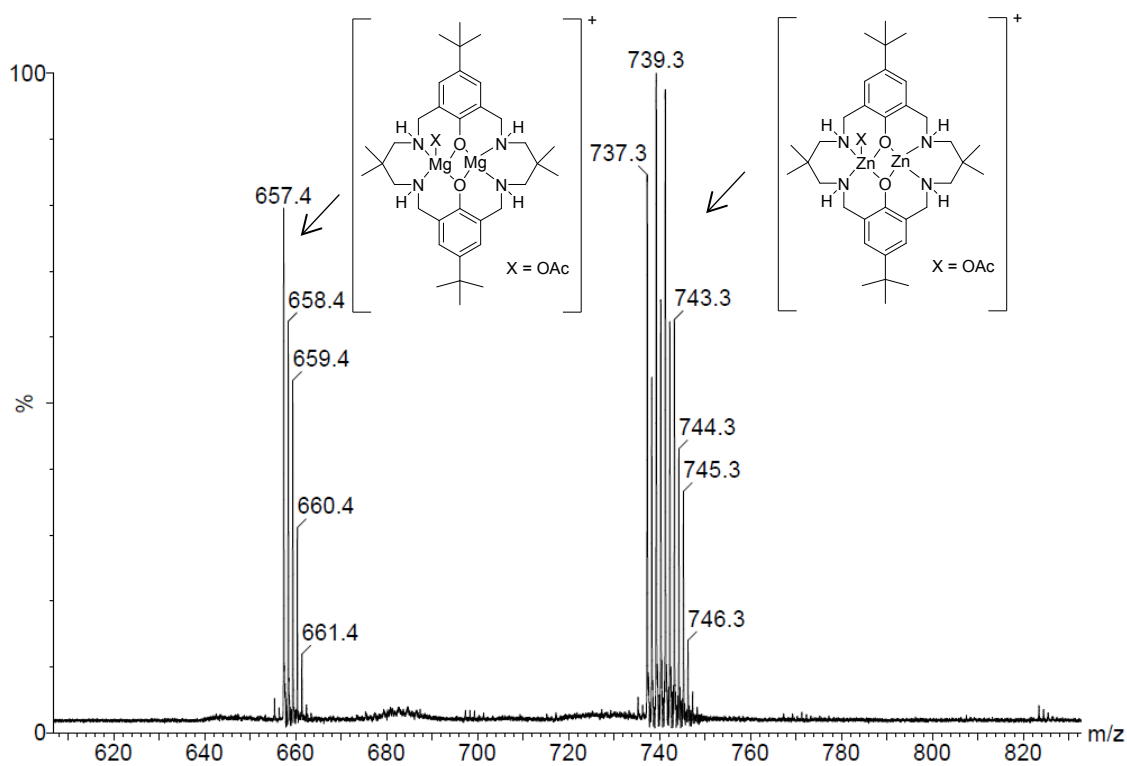


Figure S2: MALDI-ToF spectrum of 50:50 mixture of $(LZn_2(OAc)_2)$ (**1**) and $(LMg_2(OAc)_2)$ (**2**)

(2)

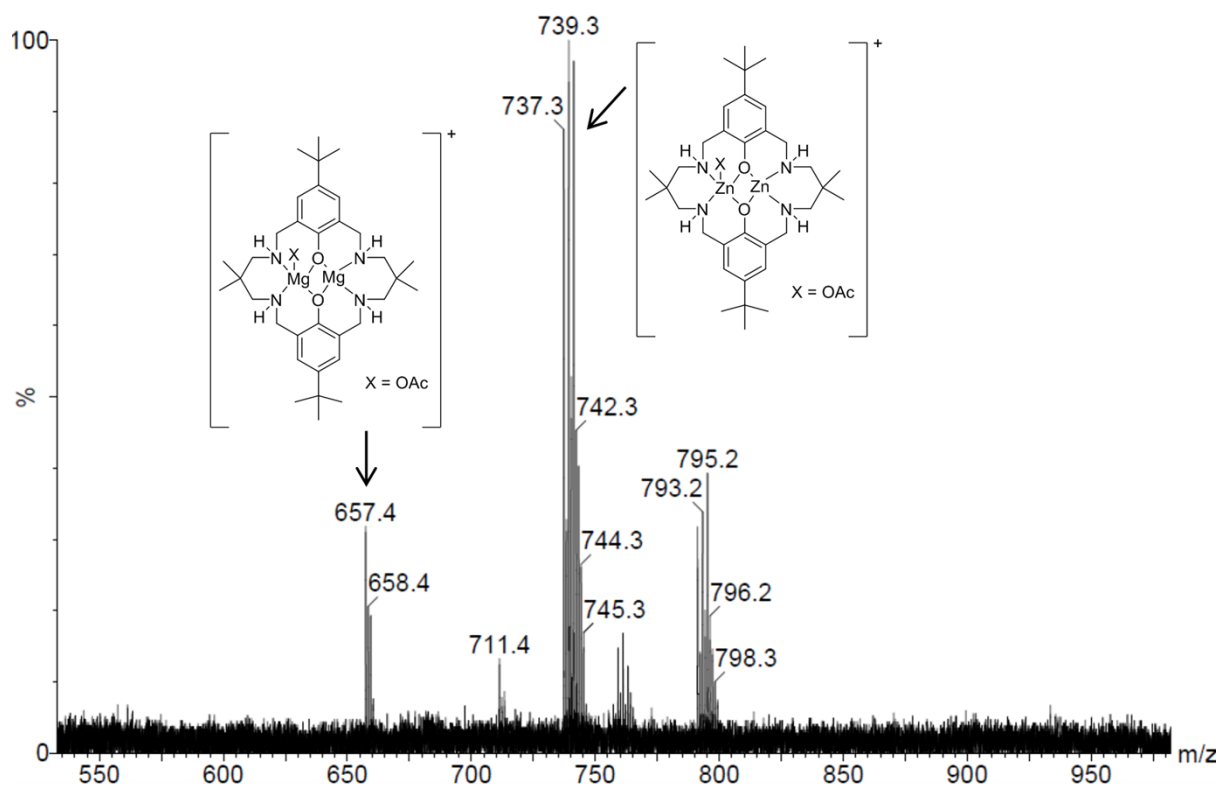


Figure S3: MALDI-ToF spectrum of 50:50 mixture of $(\text{LZn}_2(\text{OAc})_2)$ and $(\text{LMg}_2(\text{OAc})_2)$ after being heated in THF at 80 °C for 16 h. Peaks at 711 and 793 amu correspond to $[\text{LMg}_2(\text{O}_2\text{CCF}_3)]^+$ and $[\text{LZn}_2(\text{O}_2\text{CCF}_3)]^+$, respectively. These peaks arise due to the use of KTFA as a cationising agent in this experiment.

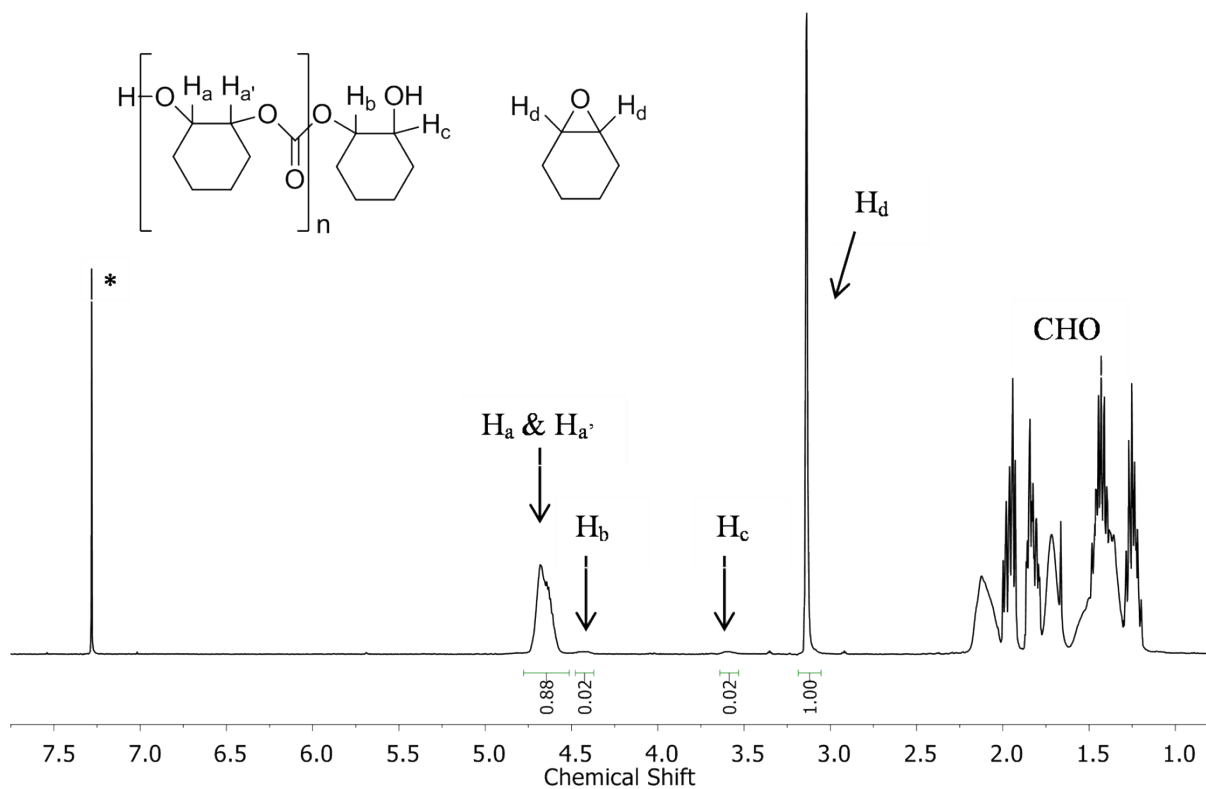


Figure S4: ^1H NMR spectrum of crude CHO/CO₂ copolymerization reaction mixture used to calculate the catalyst's TON and TOF. Also, the spectrum confirms the absence of signals due to cyclic carbonate (4 ppm) or ether linkages (3.4ppm) as by-products.

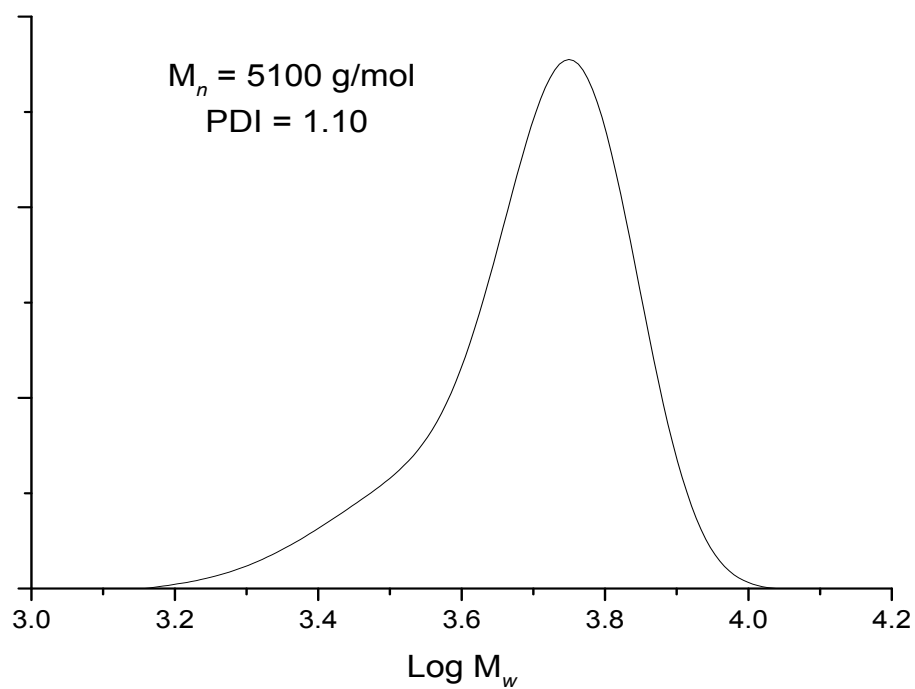


Figure S5: SEC plot (log M_w) of polycarbonate formed using catalyst system 3.

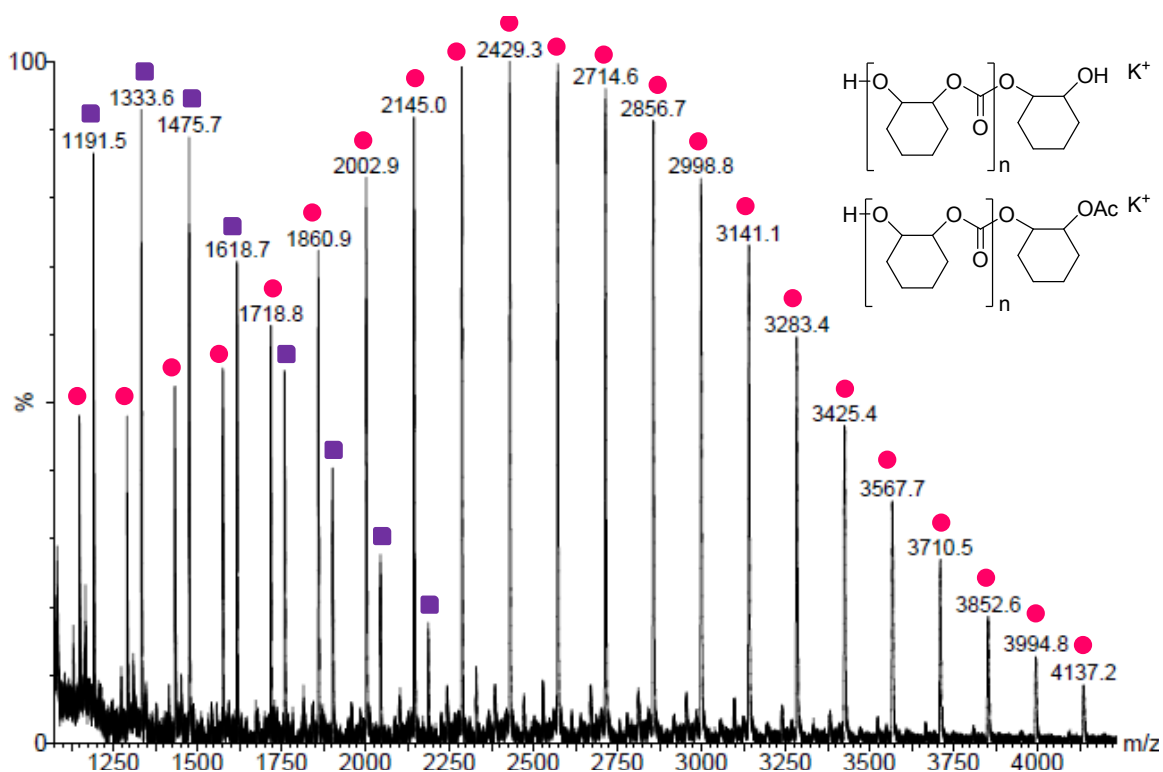


Figure S6: MALDI-ToF spectrum of the poly(cyclohexene carbonate) produced by using catalyst system 3.

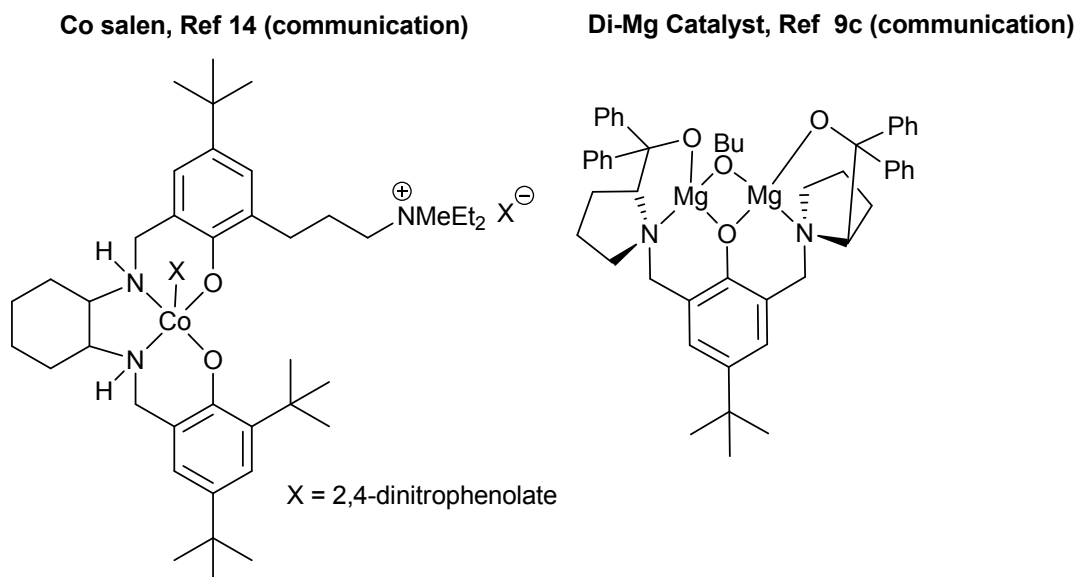


Figure S7: Illustrates the structures of the Co(salen) catalyst and di-Mg catalyst which are compared to 3 in Table 2.

Table S2: CHO/CO₂ Copolymerization data for catalyst **3 with 16 eq. of H₂O**

Catalyst 3	TON ^a	TOF (h ⁻¹) ^b	% Carbonate ^c	% Ether ^c	<i>M_n</i> (g/mol ^d)	PDI ^d
Without H₂O	286	71	>99	<1	4000	1.16
With 16 eq. H₂O	248	62	>99	<1	1300	1.14

All copolymerizations carried out in a Schlenk tube for 4h at 80 °C and 1 bar CO₂, at a 1:1000 CHO:catalyst loading. ^a The turn over number (TON) = number of moles of cyclohexene oxide consumed/number of moles of catalyst. ^b The turn over frequency (TOF) = TON/reaction period. ^c Determined by the relative integrals of the signals at 3.45 ppm (ether linkages) and 4.65 ppm (polycarbonate) ^d Determined by SEC in THF, using narrow *M_n* polystyrene standards.

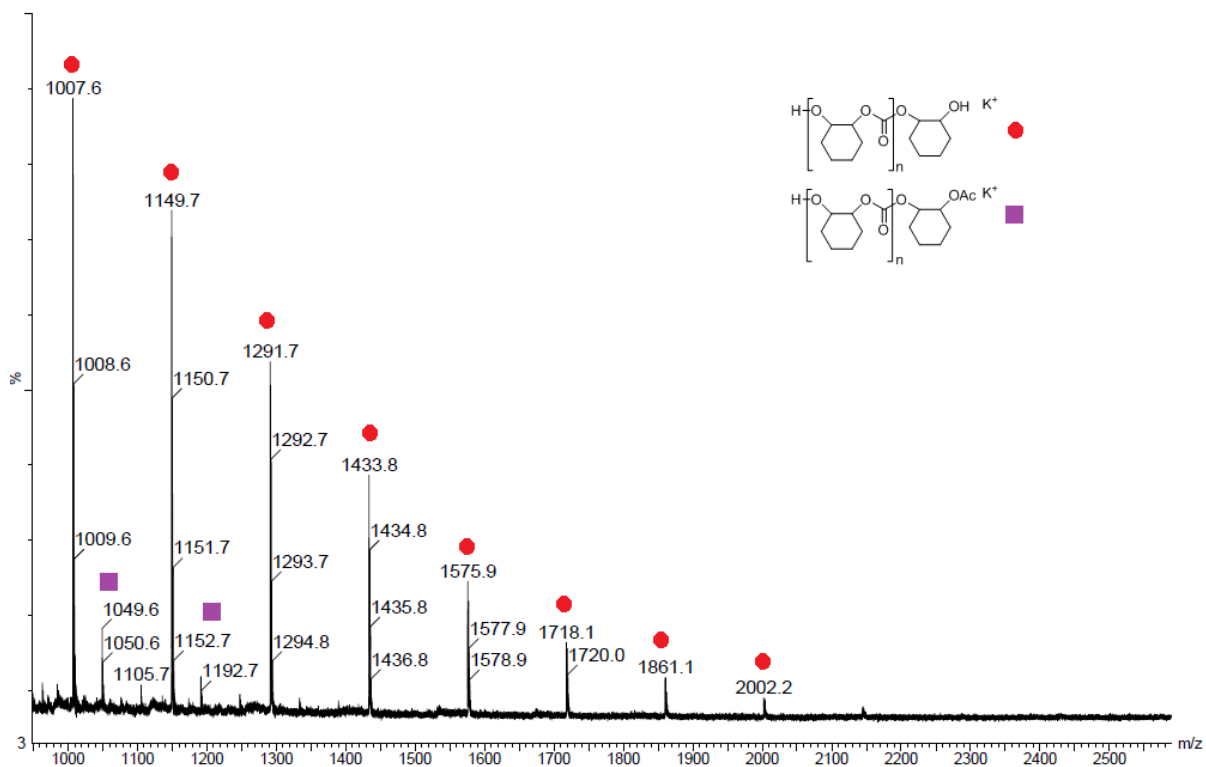
**Figure S8: MALDI-ToF spectrum of the poly(cyclohexene carbonate) produced by using catalyst system **3**, with 16 equivalents of water (Table S2, run 2).**

Table S3: PO/CO₂ copolymerization reactions with catalyst **3**

Temperature/ °C	Time/h	TON ^a	TOF (h ^{-1b})	% Conversion ^c	% PPC ^c	% PC ^c
60	22.5	248	11	25	9	91
70	22.5	435	19	44	0	>99
60*	22.5	115	5	12	0	>99

All copolymerizations conducted at 50 bar CO₂ at a 1:1000 PO:catalyst loading. ^a The turn over number (TON) = number of moles of propylene oxide consumed/number of moles of catalyst. ^b The turn over frequency (TOF) = TON/reaction period. ^c Determined by the relative integrals in ¹H NMR spectrum of crude reaction mixture 5.0 ppm (PCC), 4.85 ppm, (PC), 2.99 ppm (PO). * Copolymerization using 50:50 mixture of catalyst **1:2**.

References

1. M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem. Int. Ed.*, 2009, **48**, 931-933.
2. M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676-15679.