PAPER

Check for updates

Branched phosphazenium salts as effective and versatile cocatalysts for epoxide/CO$_2$ coupling†

Massimiliano Brivio,[a] Lorenzo Veronese,[a] Incoronata Tritto, [ID][a] Paolo Biagini,[b] Riccardo Po', [ID][b] Laura Boggioni [ID]*[a] and Simona Losio [ID]*[a]

Branched phosphazenium salts of general formula [(Me$_2$N)$_3$P=N]$_4$P$^+$X$^-$ (X$^-$ = Cl$^-$ or N$_3^-$) have been tested as cocatalysts for different catalyst systems, such as salen-type chromium and porphyrin cobalt complexes, in the alternating copolymerization of CO$_2$ and epoxides (CHO and PO) under various experimental conditions. Higher monomer conversion than that obtained with the benchmark PPN$^+$X$^-$ counterparts under the same conditions was achieved. The polymers obtained have comparable or greater molar masses. Thus, phosphazenium salts can be viable, if not superior, alternatives to onium salts in CO$_2$/epoxide ROCOP.

Introduction

Over the past decades, metal- and organocatalyzed polymerization reactions have attracted remarkable attention, leading to major advances in this field. The availability of huge combinations of both ligands and metal centers led to the rapid development of metal-based catalysts. Indeed, transition metal coordination complexes are at the heart of polymerization catalysis.[1] In the past 30 years, relevant efforts have been made for the development of homogeneous and heterogeneous catalysts for the ring opening copolymerization (ROCOP) of CO$_2$ and epoxides, such as cyclohexene oxide and propylene oxide (from now on CHO and PO, respectively).[2] This reaction is an interesting method to achieve aliphatic polycarbonates, although different amounts of cyclic by-products can be obtained.[3] Thanks to a thorough molecular design of ligands bound to metal centers, numerous catalysts show, at the same time, high activity and high selectivity towards the alternating insertion of CO$_2$ and epoxides. In all these catalytic systems involving transition metals, chain growth occurs by prior coordination of epoxides to the metal complex followed by the ring opening and formation of an alkoxide species from which the growth of the chain for alternating insertion begins as shown in Scheme 1, where X is a nucleophile coming from the cocatalyst or already present on the catalyst.[4–6]

The most investigated classes of catalytic systems consist of salen or porphyrin complexes with chromium, cobalt or aluminium as the metal together with an ionic or neutral nucleophilic co-catalyst, often 4-(*N,N*-dimethylamino)pyridine (DMAP) or soluble "onium" halide salts such as R$_4$N$^+$X$^-$ or Ph$_3$P=N$^+$=PPh$_3$ (PPN$^+$)X$^-$.

Phosphazenes are well-known organic and uncharged superbases with almost no nucleophilicity with variable numbers of phosphorus atoms and topologies (linear, branched or cyclic) (Fig. S1 in the ESI†) and have been widely studied as organocatalysts for the ring-opening polymerization (ROP) of various kinds of cyclic monomers.[7] The first known phosphazene base was synthesized in the early 1970s and had a phosphorus(v) atom with one imine group and three amine groups.[8] Due to their highly basic and non-nucleophilic nature, phosphazenes can easily turn protic compounds into nucleophilic initiators by the deprotonation or activation of weak nucleophiles, which could further initiate fast and controlled ROP reactions of various types of monomers such as epoxides.[9] Despite their relative popularity as ROP catalysts, there is a very limited number of examples of phosphazenes used in ring-opening copolymerization (ROCOP).[10,11] In 2016, different phosphazene bases have been successfully used as organocatalysts for the alternating copolymerization of epox-

[a]*CNR-SCITEC, Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", via A. Corti 12, 20133 Milano, Italy. E-mail: simona.losio@scitec.cnr.it, laura.boggioni@scitec.cnr.it*

[b]*Istituto Eni Donegani, via Fauser 4, 28100 Novara, Italy*
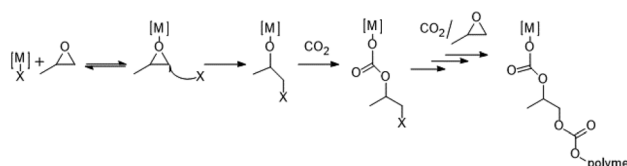
Scheme 1 Mechanism for poly(propylenecarbonate) formation.

ides and other types of monomers such as ethylene oxide or styrene oxide and 3,4-dihydrocoumarin.[12]

With regard to the copolymerization of epoxides and CO_2, the number of reported cases of phosphazene use is very small. Feng reported the effective all-organic copolymerization of cyclohexene (CHO) and propylene oxide (PO) and CO_2 with Et_3B as an initiator in the presence of phosphazenium alkoxides or phosphonium halides such as **PPNCl**.[11] Recently, in a seminal work Liu and Li reported three phosphazenes as binary organocatalysts in combination with Et_3B for the copolymerization of CO_2 and different epoxides under mild conditions.[13] Organocatalysis represents an alternative method for the synthesis of polymers under metal-free conditions, being the strategy used to manipulate the reactivity of the two monomers through their activation with a non-metal external activator such as TEB. Moreover, Coates achieved high-M_w enantiopure poly(propylene oxide) by combining tetrakis[(tri-1-pyrrolidinylphosphoranyliden)amino]phosphonium acetate with a bimetallic cobalt catalyst usually employed with CO_2.[14]

However, to the best of our knowledge, there is no available open literature to date on the use of phosphazenium salts as counterparts to the very effective PPN⁺X⁻ (X = halides or azide) cocatalyst for the synthesis of polycarbonates mediated by common monometallic catalysts. In this paper, we report the high versatility and remarkable efficiency of two P5 branched phosphazenium salts of general formula $[(Me_2N)_3P{=}N]_4P^+X^-$ (with $X^- = Cl^-$ or N_3^-), namely tetrakis[tris(dimethylamino)phosphoranylideneamino]phosphonium chloride (from now on **PPZCl**) and azide (from now on **PPZN₃**), under various synthetic conditions and in combination with different transition metal catalysts (Fig. 1). Part of this research work has been patented by some of the authors.[15]

To make a thorough comparison with **PPNX** salts and to better assess the versatility of **PPZX**, the phosphazenium salts have been tested with salen-type chromium complexes, the most known (and employed) catalysts for the two considered epoxides (Fig. 1).

Some reactions have been conducted with porphyrin cobalt complexes as well, but entirely with PO, since, according to the literature, the successful copolymerization of CHO and CO_2 to poly(cyclohexene carbonate) (from now on PCHC) is obtained with porphyrins only in the presence of neutral Lewis bases such as DMAP and not with onium salts.[16,17]
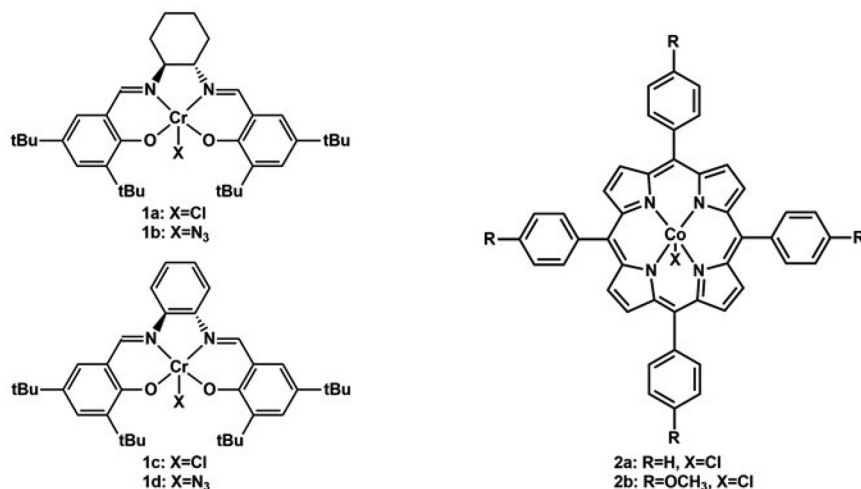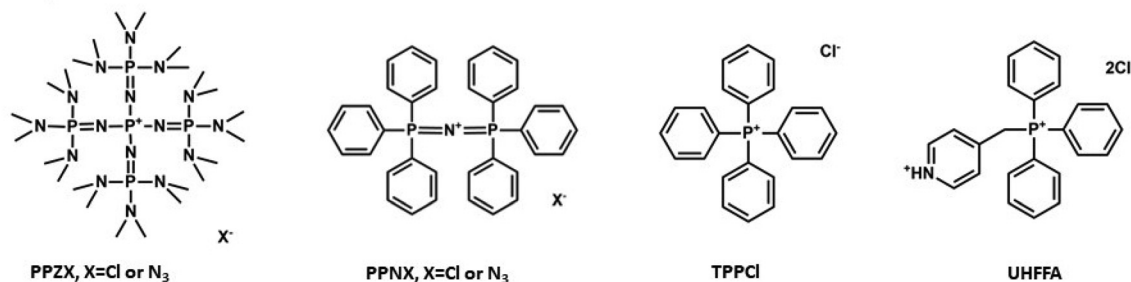

Fig. 1 Salen (**1a** and **1b**), salaphen (**1c** and **1d**) and porphyrin (**2a** and **2b**) derived metal catalysts and **PPZX**, **PPNX**, **TPPCl** and **UHFFA** cocatalysts used in this work.

Experimental

Materials and methods

Materials. Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under a nitrogen atmosphere or in a nitrogen-filled MBraun UNIlab Plus glovebox. Unless otherwise stated, all other reagents including catalyst **1a** and cocatalysts tetrakis[tris(dimethylamino)phosphoranylideneamino]phosphonium chloride (**PPZCl**), tetraphenylphosphonium chloride (**TPPCl**) and triphenyl(4-pyridinylmethyl)-phosphonium chloride hydrochloride (**UHFFA**) were received from Sigma-Aldrich and used without further purification. Dichloromethane, cyclohexene oxide and propylene oxide were freshly distilled over CaH_2. Carbon dioxide gas (99.999% purity) was purchased from Air Liquide. A deuterated solvent for NMR measurements (CD_2Cl_2) was used as received. Catalysts **1b–d** and **2a** and **b** (Fig. 1) were synthesized according to the previous literature.[18–20] **PPZN$_3$** was synthesized by adapting the reported synthesis of **PPNN$_3$**.[21]

Synthesis of tetrakis[tris(dimethylamino)phosphoranylideneamino]phosphonium azide (PPZN$_3$)

Equimolar amounts of **PPZCl** and NaN_3 were dissolved in dry EtOH under nitrogen and stirred at room temperature for at least 5 h, and then filtered to remove NaCl. The solvent was evaporated under vacuum, and the crude product was dissolved again in a few drops of CH_3CN under nitrogen and then precipitated in Et_2O, affording a pure white powder in good yield (75%). ATR (cm^{-1}): $\nu(N_3)$ 1988, $\nu(P{=}N)$ 1261. ^1H NMR (CD_2Cl_2, 300 K, 600 MHz) δ_H (ppm) 2.59 (d, 72H). Anal. calcd for $C_{24}H_{72}N_{19}P_5$: C, 36.87; H, 9.28; N, 34.04. Found: C, 36.5; H, 9.1; N, 34.8.

Alternating copolymerization of cyclohexene oxide and CO$_2$

The catalyst (1 eq.) and cocatalyst (1 eq.) were dissolved in 5 mL of CH_2Cl_2, stirred at room temperature for at least 1.5 hours, and then the solvent was removed under vacuum. 10 mL (2500 eq.) of neat cyclohexene epoxide were added to the solid residue and the solution was injected into a 25 mL steel autoclave at ambient temperature which was previously dried in vacuo at 80 °C overnight. The autoclave was charged with the desired pressure of CO_2 and heated to the reaction temperature. After a period of 3.5 h, the autoclave was cooled to room temperature and vented in a fume hood. A portion of the crude polymer was collected for NMR analysis while the rest was extracted as a dichloromethane solution and precipitated in a MeOH/HCl (9:1) solution. The purification process was repeated three times and the purified polymer was dried in vacuo at 80 °C overnight.

Alternating copolymerization of propylene oxide and CO$_2$

The catalyst (1 eq.) and cocatalyst (0.5 eq.) were dissolved in 5 mL of CH_2Cl_2 and stirred at room temperature for at least 1.5 hours, and then the solvent was removed under vacuum. 10 mL (2500 eq.) of neat propylene epoxide were added to the solid residue and the solution was added via the injection port into a 25 mL steel autoclave at ambient temperature which was previously dried in vacuo at 80 °C overnight. The autoclave was charged with the desired pressure of CO_2 and heated to the reaction temperature. After the designed reaction time, the autoclave was cooled to room temperature and vented in a fume hood. A portion of the crude polymer was immediately collected and frozen for NMR analysis, while the rest was extracted as a dichloromethane solution and precipitated in a MeOH/HCl (9:1) solution. The so-obtained polymer was dissolved again in dichloromethane and precipitated in diethyl ether two times, and then the purified polymer was dried in vacuo at 40 °C overnight.

Polymer characterization

All the ^1H and ^{13}C NMR spectra were recorded on a Bruker DMX 600 MHz NMR spectrometer in CD_2Cl_2 at 300 K. Infrared spectra (FTIR-ATR) were recorded on a PerkinElmer Spectrum Two spectrometer. Size exclusion chromatography (SEC) analyses were performed on a Waters GPCV2000 system using THF as the mobile phase at 35 °C with a 0.6 mL min^{-1} flow. The sample concentration was set at 3 mg mL^{-1} and the injection volume at 150 μL. Polystyrene standards were used for the calibration of curves in the 162–380 000 g mol^{-1} range. Calorimetric curves were obtained using a PerkinElmer DSC 8000 under a nitrogen atmosphere, with the samples being heated from −80 to 150 °C and cooled vice versa twice at 20 °C min^{-1}. Analytical elemental analyses were performed at the Department of Chemistry, Materials and Chemical Engineering (CMIC) at Politecnico di Milano.

Results and discussion

In spite of their widespread use as catalysts for epoxide homopolymerization, phosphazenium salts are almost unknown as cocatalysts for the ROCOP of epoxides and CO_2 and only a very few examples of their use do exist in the literature.[11,14] One of the most interesting examples of such a use of phosphazenium salts dates back to 2016, when Feng used Et_3B and phosphazenium benzyloxides, generated in situ from t-Bu-Pn phosphazene bases and benzyl alcohol, to couple cyclohexene oxide or propylene oxide with CO_2.[11] In this work, a comparison between phosphazenium alkoxides and PPN halides is made, but no reaction using a phosphazenium halide is mentioned. Moreover, the resulting poly(propylene carbonate) (from now on PPC) and poly(cyclohexene carbonate) showed rather moderate TONs and molar masses compared to those obtained, within the same work, with other cocatalysts.

The choice for this investigation then fell upon two salts of the large branched P5 $[(Me_2N)_3P{=}N]_4P$ (PPZ) phosphazene, namely its chloride and its azide, the two most largely used anions of PPN salts. The phosphazenium salts have been tested for PO and CHO copolymerization with salen-type chromium complexes, and only for PO copolymerization with porphyrin cobalt complexes (Fig. 1).

Copolymerization of CO$_2$ and cyclohexene oxide (CHO) catalyzed by chromium(III) salen complexes

In Table 1, the results of the copolymerization of CHO and CO_2 with salen-type catalysts **1a** and **1b** and **PPZX** cocatalysts are sum-

Table 1 Comparison of CHO and CO$_2$ copolymerization results with salen-type catalysts **1a** and **1b** and PPZX or PPNX as the cocatalyst[a]

Entry	Catalyst	Cocatalyst	Conversion[b] (%)	Selectivity[b] (%)	Ether linkage[b] (%)	TON[c]	$M_n{}^d$ (g mol^{-1})	Theoretical $M_n{}^e$	$Đ^d$	$T_g{}^f$ (°C)
1[g]	**1a**	**PPNCl**	65	>99	—	1625	13 300	79 625	1.1	119
2[h]		**PPZCl**	85	>99	—	2125	14 385	104 125	1.1	117
3		**PPNN$_3$**	85	>99	2.8	2125	9400	104 125	1.3	117
4[g]		**PPZN$_3$**	86	>99	1.6	2150	14 200	105 350	1.2	119
5	**1b**	**PPNCl**	85	>99	1.5	2125	9800	104 125	1.1	116
6[h]		**PPZCl**	83	>99	1.8	2075	13 100	101 675	1.2	118
7		**PPNN$_3$**	83	>99	1.8	2075	8800	101 675	1.2	111
8		**PPZN$_3$**	84	>99	1.0	2075	12 600	102 900	1.1	118

[a] Catalyst : cocatalyst : CHO = 1 : 1 : 2500, T = 80 °C, P_{CO_2} = 30 bar, and t = 3.5 h. [b] Determined by ^{1}H NMR spectroscopy of the crude product; conversion = moles of epoxide reacted, and selectivity = moles of polymer over cyclic carbonate. [c] Moles of CHO consumed per mole of Cr. [d] Determined by SEC using a polystyrene standard. [e] Theoretical M_n = [conversion ratio (catalyst : CHO) × 98 g mol^{-1}]/2. [f] Determined from the DSC second heating cycle. [g] From ref. 22a. [h] Continuous flow of CO$_2$.

marized and compared with those obtained with the two onium PPN$^+$ counterparts, used here as reference cocatalysts.

All the reactions were carried out first in neat epoxide at 80 °C at 30 bar of CO$_2$ for 3.5 hours, that is under the best conditions found in our study for the same copolymerization with the **PPNCl** cocatalyst.[22a] A pretreatment between the Cr(III) complex and the ionic phosphazene derivative was always carried out prior to copolymerization to ensure the maximum catalytic activity, by dissolving and stirring them in CH$_2$Cl$_2$ for a few hours, followed by removal of the solvent under vacuum. Reactions were generally performed by pressurizing CO$_2$ to the desired pressure in the reactor and then leaving the polymerization medium stirring at a fixed temperature.[22]

When catalyst **1a** (salenCrCl) is used, the employment of **PPZCl** with respect to **PPNCl** affords a remarkable improvement in the conversion, and subsequently in the TON, and only a slight increase in the molar mass is observed. The comparison of copolymers obtained with **PPZN$_3$** *vs.* **PPNN$_3$** reveals a significant improvement in the molar mass given by the phosphazenium PPZ cation. The use of catalyst **1b** (salenCrN$_3$) allows instead a more stable trend in the conversion, which remains high, over 80%, with any cocatalyst. In this case, the advantage brought by the use of phosphazenium salts is visible in the increase of molar mass, affording copolymers with molar masses greater than a few thousand g mol^{-1}. Along with remarkable conversions, selectivities also remain always higher than 99%, with the production of polycarbonate and a complete absence of cyclic carbonate and, with **1a** and **PPZCl**, no or very few ether linkages, as clearly seen in the ^{1}H NMR spectra of the crude products (Fig. S2 in the ESI†), completely flat in the 4.4–3.1 ppm region. Moreover, some polyether linkages, up to 1.8 mol%, are formed with all the cocatalysts and catalyst **1b** (Fig. S3 in the ESI†). A narrow but bimodal dispersity of polycarbonates, determined by SEC measurements, is observed, indicating that the polymers have two distinct molar masses with each molar mass profile displaying a narrow dis-

persity (Fig. S4 in the ESI†). This dispersity may be due to a rapid and reversible chain transfer caused by trace amounts of water in the reaction mixture.[23,24] The effectiveness of chain transfer is confirmed by the well-known discrepancy between the expected polymer M_n and that actually measured. The polydispersity indices are narrow and indicate that the chain transfer reactions occur more rapidly than propagation. The thermal analysis of the obtained samples shows T_gs values of around 111–119 °C, in agreement with those previously reported for pure PCHC (Fig. S5 in the ESI†).[25]

It is well known that ionic cocatalysts cannot affect the stereoselectivity of copolymerization. Indeed, only some salenCrX catalysts were found able to stereospecifically desymmetrize *meso*-epoxides; specifically, **1a** was reported to be active only in the desymmetrization of 1-hexene,[26] while CHO could only be partially (14.5 ee%) desymmetrized with S,S-salen-CrNO$_3$ in the presence of N-heterocyclic Lewis bases.[27] Thus, in our case only atactic polymers were in fact obtained, with the syndio and iso peaks each accounting for *ca.* 50% of the total signals in the ^{13}C NMR spectrum as shown in Fig. 2.[28]

PPZCl has been studied at different temperatures (Table 2) with catalyst **1a** to identify the effect of reaction conditions on conversion, molar mass, and selectivity. At 60 °C under our conditions, low conversion of the epoxide, around 17%, can be observed. It is clear that at such a temperature, the kinetics of the copolymerization is too slow. As the temperature is increased, the catalytic performance improves, and thus the best results in terms of CHO conversion and selectivity of polycarbonates are obtained at 80 °C both with **PPZCl** and **PPNCl** cocatalysts.[22a] In general, upon increasing the temperature, conversion and selectivity decrease. This trend is similar to that observed with **UHFFA**.[22a] Molar masses are low only at 60 °C (Fig. S6 in the ESI†). The lower T_g values observed at high temperatures may be related to lower selectivities (Fig. S7 in the ESI†).
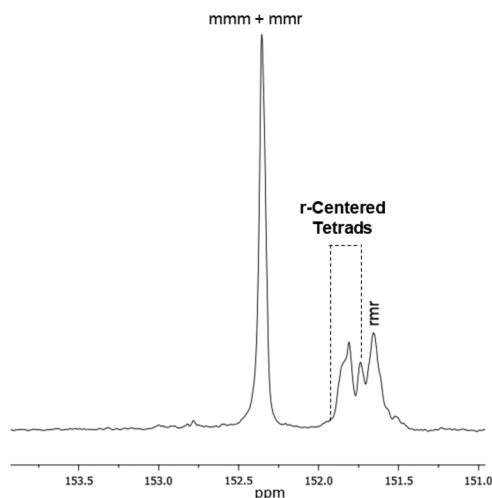
Fig. 2 ^{13}C NMR spectrum of PCHC (Table 1, entry 2), in which the signals due to the C=O groups of the carbonate group appear.

Salaphen catalysts, **1c** and **1d**, were also tested, although as already reported by Darensbourg *et al.*,[18] in combination with other cocatalysts, their electron-poor diimine backbone is less effective with CHO, leading to much lower conversions and to copolymers with much lower molar masses. This remains true in any case, and even the usage of high performing **PPZX** phosphazenium salts cannot overcome the drawbacks caused by the catalyst skeleton, leading to halved conversions (*ca.* 45%

and 40%) and molar masses (*ca.* 7000 g mol^{-1} and 5600 g mol^{-1}) with **PPZCl** and **PPZN$_3$**, respectively, also producing a tiny but finite amount, about 2–3 mol%, of cyclic carbonate. The presence of a Cl group rather than a N$_3$ nucleophilic group on the catalyst or the cocatalyst leads to minimum differences that can be easily neglected.

Copolymerization of CO$_2$ and propylene oxide (PO) catalyzed by chromium(III) salaphen complexes

It is well recognized that, depending on the monomer, different salen-type catalysts should be used, due to the electronic effect of the skeleton. In particular, electron-rich diamine backbones are highly efficient with CHO, while with PO no reaction occurs or only a cyclic carbonate is formed.[29,30] Metal complex catalysts with electron poor aromatic rings are very effective with PO, and thus catalysts **1c** and **1d** have been used in the copolymerization of propylene oxide and CO$_2$ to study the phosphazenium salts as cocatalysts.

All of the copolymerization reactions were carried out in neat epoxide at 60 °C, at 30 bar of CO$_2$, for 24 h. A catalyst to cocatalyst ratio of 1 : 0.5 has been used to afford the best polymerization rate, according to the results reported in our previous paper.[22a] The copolymers were characterized by ^1H NMR spectroscopy and SEC analysis and the main results are presented in Table 3.

In general, good results in terms of conversion, selectivity and molar mass are obtained with all cocatalysts. Conversion values vary considerably and increase when PPZ salts are used;

Table 2 Copolymerization reaction of CHO and CO$_2$ with catalyst **1a** and **PPZCl** at different temperatures^a

Entry	T (°C)	Conversion^b (%)	Selectivity^b (%)	TON^c	M_n^d (g mol^{-1})	$Ð^d$	Theoretical M_n^e	T_g^f (°C)
9	60	17	>99	425	4500	1.2	20 825	110
2	80	85	>99	2125	14 385	1.1	104 125	117
10	100	76	93	1900	15 900	1.2	93 100	114
11	120	75	88	1875	15 700	1.3	91 875	113

^{a} Catalyst = **1a**, cocatalyst = **PPZCl**, catalyst : cocatalyst : CHO = 1 : 1 : 2500, P_{CO_2} = 30 bar, and t = 3.5 h. ^{b} Determined by ^1H NMR spectroscopy of the crude product; conversion = moles of epoxide reacted, and selectivity = moles of polymer over cyclic carbonate. ^{c} Moles of CHO consumed per mole of Cr. ^{d} Determined by SEC using a polystyrene standard. ^{e} Theoretical M_n = [conversion ratio (catalyst : CHO) × 98 g mol^{-1}]/2. ^{f} Determined from the DSC second heating cycle.

Table 3 Comparison of PO and CO$_2$ copolymerization results with salaphen-type catalysts **1c** and **1d** and **PPZX** or **PPNX** as the cocatalyst^a

Entry	Catalyst	Cocatalyst	Conversion^b (%)	Selectivity^b (%)	Ether linkage^b (%)	TON^c	M_n^d (g mol^{-1})	Theoretical M_n^e	$Ð^d$	T_g^f (°C)
12	**1c**	**PPNCl**	78	76	—	1950	38 500	56 550	1.2	38
13		**PPZCl**	82	82	—	2050	41 000	59 450	1.2	42
14		**PPNN$_3$**	78	80	—	1950	30 700	56 550	1.2	40
15		**PPZN$_3$**	84	82	—	2100	38 200	60 900	1.2	42
16^g	**1d**	**PPNCl**	73	64	10	1800	26 000	52 925	1.3	34
17		**PPZCl**	79	85	5	1975	32 300	57 275	1.3	38
18		**PPNN$_3$**	58	89	—	1450	20 771	42 050	1.2	41
19		**PPZN$_3$**	88	99	6	2200	29 200	63 800	1.2	35

^{a} Catalyst : cocatalyst : PO = 1 : 0.5 : 2500, T = 60 °C; P = 30 bar, and t = 24 h. ^{b} Determined by ^1H NMR spectroscopy of the crude product; conversion = moles of epoxide reacted, and selectivity = moles of polymer over cyclic carbonate. ^{c} Moles of PO consumed per mole of Cr. ^{d} Determined by SEC using a polystyrene standard. ^{e} Theoretical M_n = [conversion ratio (catalyst : PO) × 58 g mol^{-1}]/2. ^{f} Determined from the DSC second heating cycle (Fig. S8 in the ESI†). ^{g} From ref. 22a.
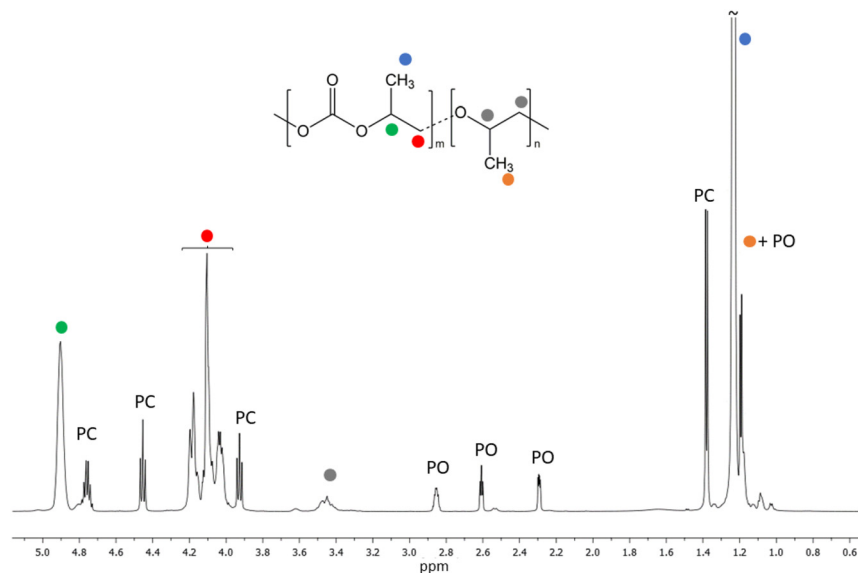
Fig. 3 ^1H NMR spectrum of the obtained crude PPC (Table 3, entry 17). Signals assigned to cyclic propylene carbonate (PC) and unreacted PO signals are visible.

moreover, a certain percentage of polyether is always obtained in all samples from **1d**, that is with the salaphen catalyst having N_3 as a ligand, as shown in Fig. 3 by the ^1H NMR peak at 3.5 ppm (Fig. S9 and S10 in the ESI†). **PPZN$_3$** showed the greatest selectivity toward polycarbonate formation (99%) (Table 3, entry 19). Molar masses greater than those obtained with the benchmark **PPNX** are obtained with **PPZCl**, and M_n values of 41 000 and 32 300 g mol^{-1} are obtained with catalyst **1c** and **1d**, respectively (Table 3, runs 13 and 17, and Fig. S11 in the ESI†).

Copolymerization of CO$_2$ and propylene oxide (PO) catalyzed by cobalt(III) porphyrin complexes

Cobalt(III) tetraphenylporphyrin chloride (TPPCoCl) has been proved to be an active catalyst for the alternating copolymerization of CO$_2$ with both CHO and PO, as first discovered by Wang[31] and Sugimoto.[16] Later, modifications of the porphyrin

ligand with the introduction of a series of electron-withdrawing groups in the *para*-position of the *meso*-ring showed a slight increase in the catalytic activity in the copolymerization of CO$_2$ with PO.[20]

Thus, we decided to perform some PO/CO$_2$ copolymerization reactions in the presence of **PPZCl** with **2a**, the prototypical TPPCoCl, and **2b**, [5,10,15,20-tetra(*para*-methoxy) phenylporphyrin]cobalt(III) chloride, catalysts and to compare the polymerization results with those obtained with the benchmark **PPNCl** (Table 4). In addition, some reactions have been conducted with two quaternary phosphonium salts, namely **TPPCl** and **UHFFA** (Fig. 1), recently reported as effective cocatalysts in the alternating copolymerization of carbon dioxide with epoxides.[20] Both these cocatalysts in combination with N,N'-bis(3,5-di-*tert*-butylsalicylidene)-phenylenediimine chromium(III) azide exhibit catalytic activity with PO (in neat epoxide at 60 °C, P = 30 bar, t = 24 h), with tetraphenylpho-

Table 4 Comparison of PO and CO$_2$ copolymerization results with porphyrin-type **2a and 2b** catalysts and different cocatalysts[a]

Entry	Catalyst	Cocatalyst	Conversion[b] (%)	Selectivity[b] (%)	Ether linkage[b] (%)	TON[c]	M_n[d] (g mol^{-1})	Theoretical M_n[e]	Đ[d]	T_g[f] (°C)
20	**2a**	**PPNCl**	60	93	7	1500	34 300	43 500	1.1	—
21		**PPZCl**	67	34	7	1675	56 400	48 575	1.4	43
22		**PPZN$_3$**	65	41	14	1425	32 570	47 125	1.3	41
23		**TPPCl**	28	>99	—	700	10 900	20 300	1.1	36
24		**UHFFA**	22	>99	—	550	17 100	15 950	1.1	40
25	**2b**	**PPNCl**	71	66	7	1775	40 700	51 475	1.3	41
26		**PPZCl**	90	66	11	2250	54 500	65 250	1.3	42
27		**PPZN$_3$**	75	41	8	1875	49 500	54 375	1.4	40
28		**TPPCl**	75	64	25	1875	34 200	54 375	1.3	40
29		**UHFFA**	42	>99	—	1050	15 200	30 450	1.1	35

[a] Catalyst : cocatalyst : PO = 1 : 0.5 : 2500, T = 25 °C; P = 20 bar, and t = 24 h. [b] Determined by ^1H NMR spectroscopy of the crude product; conversion = moles of epoxide reacted, and selectivity = moles of polymer over cyclic carbonate. [c] Moles of PO consumed per mole of Cr. [d] Determined by SEC using a polystyrene standard (Fig. S12 in the ESI†). [e] Theoretical M_n = [conversion ratio (catalyst : PO) × 58 g mol^{-1}]/2. [f] Determined from the DSC second heating cycle (Fig. S13 in the ESI†).

sphonium chloride affording the best results in terms of selectivity, exceeding the values obtained with the reference **PPNCl** cocatalyst.

The copolymerization reactions have been conducted at 20 bar of CO_2 pressure, at 25 °C, and for 24 hours (Table 4). These conditions have been chosen since by increasing the reaction temperature and CO_2 pressure, a gradual loss of the catalytic activity can be observed; moreover, at higher temperatures, the formation of cyclic carbonate due to the chain-back biting reaction increases.[16,31]

Of all the analyzed cocatalysts, **TPPCl** and **UHFFA** show a detrimental effect on the conversion and molar mass, but

show high selectivity in PPC copolymerization with **2a** as a catalyst, compared with **PPNCl**. In contrast, the presence of electron-donating fragments in the **2b** catalyst has a beneficial effect on the catalytic activity of this complex, with the classical **PPNCl**, the phosphazenium salt and the **UHFFA** cocatalyst, since the introduction of the methoxy group modulates the electronic environment at the cobalt center, increasing the copolymer yield compared with that from the unsubstituted **2a** catalyst. These results are in agreement with those reported by Rieger with a series of 5,10,15,20-tetra(*p*-alkoxy)porphyrin cobalt(III) chlorides and by Inoue for Al-porphyrins substituted with methoxy groups.[20,32] A similar increase in the catalyst activity has been reported by Darensbourg with the introduction of methoxy groups into the salen-phenolate rings.[18]

In addition, moving from phosphonium to phosphazenium salt, both catalysts exhibit a sensible increase in the molar mass, above 54 000 g mol^{-1}, when **PPZCl** is used. With catalyst **2a** and both cocatalysts slightly higher conversions are achieved even with significantly lower selectivity, while with catalyst **2b**, higher conversion with no changes in the selectivity can be observed with **PPZCl** (Fig. S14–S17 in the ESI†).

The quaternary phosphonium salts show for both catalysts a clear decrease in the conversion along with a sensible increase in the selectivity up to 99 mol%; however, molar masses up to 17 000 g mol^{-1} are obtained. It is worth noting that in light of the low conversion, the obtained molar masses, even though lower than those observed with salen catalysts, show a value of about 50% of the theoretical M_n value.

Comparison of the effects of branched phosphazenium salts as cocatalysts on the copolymerization of CO_2 and CHO and PO

In order to find a rationale for the effects of branched phosphazenium salts as cocatalysts on the copolymerization of CO_2 and CHO and PO, M_n vs. conversion profiles for copolymerization of CHO with salen-type catalysts **1a** and **1b** and for PO copolymerization with salaphen-type catalysts **1c** and **1d** and different cocatalysts are compared in Fig. 4. For this compari-
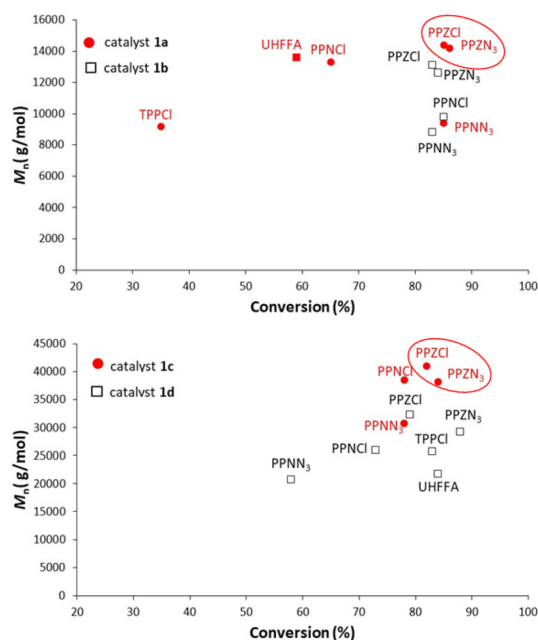

Fig. 4 M_n vs. conversion of CHO copolymerization with salen-type catalysts **1a** and **1b** (top) and of PO copolymerization with salaphen-type catalysts **1c** and **1d** (bottom) and different cocatalysts.
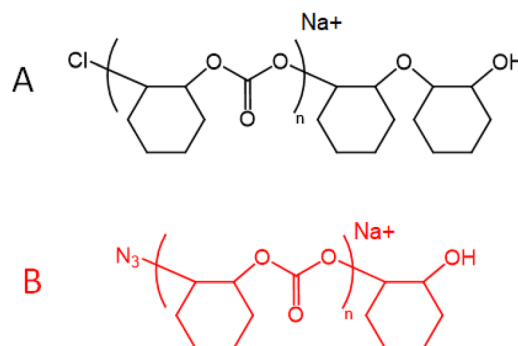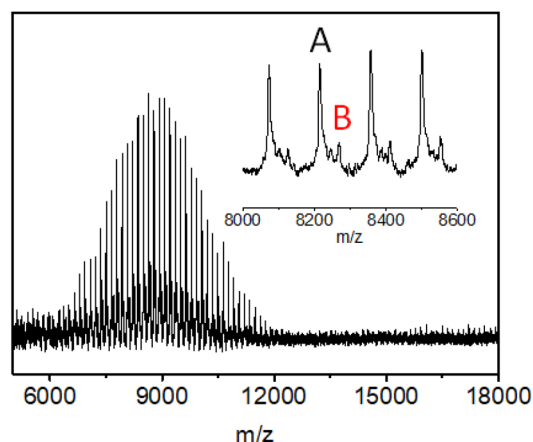

Fig. 5 MALDI-TOF spectrum collected for entry 8 (zoomed in from m/z = 8600 to m/z = 9000), prepared with catalyst **1b** and **PPZN$_3$** as a cocatalyst.

son, our data obtained under the same conditions but with cocatalysts different from those shown in Tables 1–3 have also been included.[22a]

It is evident that higher molar masses and monomer conversion with PPZ^+X^- than those with the benchmark PPN^+X^- counterparts under the same conditions are achieved. These differences are more visible in PO copolymerization, which shows higher molar mass than CHO copolymerization. We hypothesized that greater molar masses of PO copolymers are due to the lower propensity of PO towards chain transfer.[22a] It is also evident that **PPZCl** gives better results than **PPZN₃**, in terms of molar mass, and **PPZN₃**, in terms of conversion. Moreover, in

general with both **PPZX** salts and chlorine catalysts salenCrCl (**1a**) and salaphenCrCl (**1c**), better copolymer results than with salenCrN₃ (**1b**) and salaphenCrN₃ (**1d**) are obtained.

MALDI-ToF-MASS spectra may be helpful to demonstrate which is the end group or real initiator and to better understand the polymerization mechanism. An investigation of the effect of different catalytic systems on the chain structures and end groups of CO₂-based polycarbonates by MALDI-TOF mass spectrometry has been carried out. The spectra are complex and the discussion of results is the object of a manuscript in preparation.[35] However, in Fig. 5, the MALDI-TOF spectrum collected for entry 8, prepared with catalyst **1b** and **PPZN₃** as a cocatalyst, is shown.

Two signals named A and B, one end-capped with a chloride group and a hydroxyl group and the other one with a hydroxyl group and an azide, can be observed. Although N₃ is present on both the catalyst **1b** and cocatalyst (entry 8 in Table 1) signal B is the smallest. The presence of Cl at one end probably originates from the pretreatment of the catalyst and cocatalyst in dichloromethane.[23] The presence of the high A signal is a clear indication that there is an equilibrium between the N₃ anion and Cl and that the equilibrium is shifted towards chlorine.

Regarding selectivities in CHO copolymerization, all cocatalysts used in this work show selectivities over 99%, while selectivities vary considerably in PO copolymerization (Fig. 6). In these copolymerization reactions, there is an almost direct relationship between monomer conversion and selectivity.
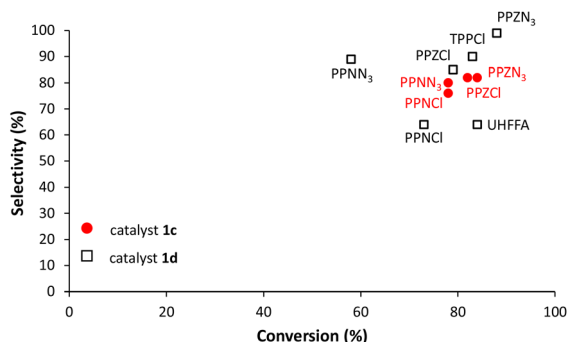

Fig. 6 Selectivity vs. conversion of PO copolymerization with salaphen-type catalysts **1c and d** and different cocatalysts.
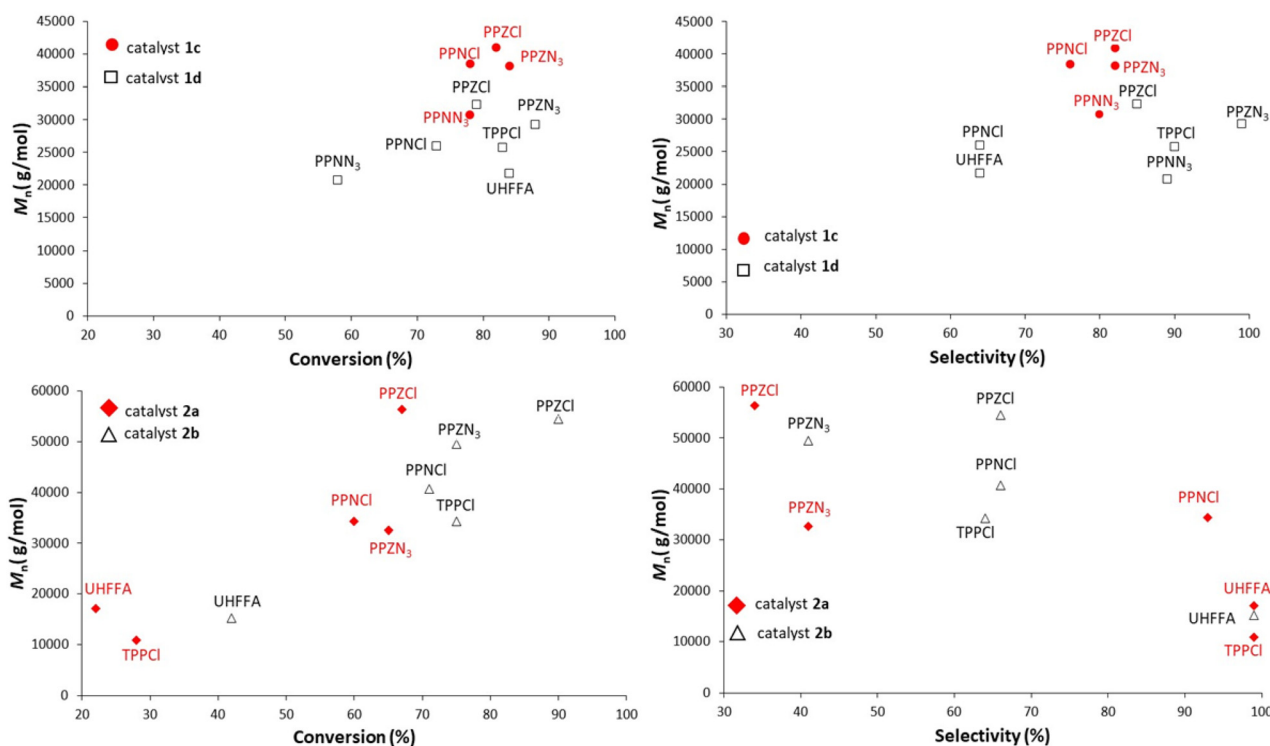

Fig. 7 M_n vs. conversion (left) and vs. selectivity (right) of PO copolymerization with salaphen-type catalysts **1c and 1d** (top) and with porphyrin-type **2a and 2b** catalysts and different cocatalysts (bottom).

Interestingly **PPZN₃** which exhibits the highest conversion gives the highest selectivity with salaphenCrN₃ (**1d**).

This confirms our previous observation that cocatalysts less efficient in PO copolymerization have lower selectivities and/or higher ether linkages.

This behavior was explained by considering that with less effective cocatalysts polymeric species spend more time in the resting state, which makes more probable the formation of cyclic carbonate and ether linkages (Scheme S1 in the ESI†).[35]

Comparison of the results of PO copolymerization with porphyrins in Fig. 7 is more difficult to rationalize at first sight.

However, porphyrin catalysts also give better results with **PPZX** cocatalysts than with **PPNX** cocatalysts. Moreover, if we consider only the results obtained with branched **PPZX** cocatalysts, **PPZCl** and **PPZN₃** give a very high molar mass with catalyst **2b** and **PPZCl** gives the same also with catalyst **2a**. Moreover, for the same copolymerization there is again a correspondence between selectivities and conversion. It is not clear if results with **PPZN₃** and catalyst **2a** are outliers.

UHFFA, **TPPCl**, and **PPNCl** give the highest selectivities with porphyrin catalysts, but give lower conversions and molar masses. Probably steric hindrances of catalysts and cocatalysts play a role in these copolymerization reactions.

Copolymerization of epoxides and CO_2 involves the coordination of the epoxide to the metal activated by X, a nucleophile coming from the cocatalyst, which favours the epoxide insertion by facilitating the removal of the catalyst ligand Nu (Scheme S1 in the ESI†). If we consider ionic cocatalyst salts such as PPN⁺X⁻ and PPZ⁺X⁻ where X⁻ is Cl or N_3, the following equilibria have to be taken into account:

$$PPZ^+X^- \rightleftharpoons PPZ^+ + X^-$$

$$PPN^+X^- \rightleftharpoons PPN^+ + X^-$$
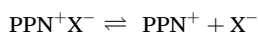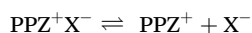
The size of the cation influences the strength of the anion–cation interaction. PPZ⁺ has greater steric hindrance (see Table S1 in the ESI†) and greater ability to stabilize the positive ion pair than PPN⁺ which shifts the above equilibria more to the right, allowing X⁻ to activate the metal of the catalyst. This difference seems to explain the greater efficiency of branched phosphazenium salts as cocatalysts. The influence of the size of the cation on the propagation rate and thus on the activity and selectivity is quite common for anionic ROP.[36]

Conclusions

Large branched phosphazenium salts of general formula $[(Me_2N)_3P=N]_4P^+X^-$, where X is chloride or azide, the two most largely used anions of PPN salts, have been tested as cocatalysts for different catalyst systems in the alternating copolymerization of CO_2 and CHO with salen-type chromium complexes, salenCrCl (**1a**) and salenCrN₃ (**1b**), under various experimental conditions. A careful examination of the catalytic activity of the various complexes and of the molar mass indicated that the use of **PPZX** salts as cocatalysts has a beneficial

effect on the copolymer production, with conversions at least comparable or even superior to those obtained from onium salts. Higher monomer conversion and greater molar masses than those obtained with the benchmark PPN⁺X⁻ counterparts under the same conditions were achieved. **PPZCl** gives better results than **PPZN₃** in terms of molar mass, and **PPZN₃** in terms of conversion, and in general with both **PPZX** salts, salenCrCl (**1a**) gives better copolymerization results than salenCrN₃ (**1b**).

The phosphazenium salts have also been tested for PO and CO_2 copolymerization with salaphenCrCl (**1c**) and salaphenCrN₃ (**1d**), as well as with porphyrin cobalt complexes tetra phenylporphyrinCoCl (**2a**) and the tetramethoxysubstituted one (**2b**). With both cocatalysts higher molar masses and comparable or even superior conversions and selectivities are mostly obtained with respect to the onium cocatalysts. In particular, when porphyrin catalysts are used, molar masses above 50 000 g mol⁻¹ are achieved. Thus, phosphazenium salts are viable, or even superior, alternatives to onium salts in CO_2/epoxide ROCOP.

If we consider the reaction mechanisms proposed by Darensbourg[33] and Coates,[34] cations which are able to easily delocalize positive charge should be the most active for the copolymerization, because of better stabilization of the separated ion pair. Moreover, the phosphazenium positive effect is also probably due to their higher steric hindrance that favours the epoxide's interaction with the catalyst and subsequently its ring opening. It is well known that the epoxide ring opening is the rate-determining step. In conclusion, the greater possibility of phosphazenium cations to delocalize the positive charge due to their conjugated double bond structure along with the great steric hindrance of the bulky branched structure allow them to overcome onium cations.

Author contributions

M. Brivio and L. Veronese, investigation; P. Biagini and R. Po', conceptualization and validation; I. Tritto, writing – review and editing; and S. Losio and L. Boggioni, supervision, conceptualization, writing – review and editing.

Conflicts of interest

The patent WO2020229965A1 covers part of the work presented in this paper.

Acknowledgements

Notes and references

1 (a) M. Bochmann, *Organometallics*, 2010, **29**, 4711; (b) N. Ajellal, J.-F. Carpentier, C. Guillaume, S. M. Guillaume, M. Helou, V. Poirier, Y. Sarazin and A. Trifonov, *Dalton Trans.*, 2010, **39**, 8363; (c) Z. Hou and Y. Wakatsuki, *Coord. Chem. Rev.*, 2002, **231**, 1.

2 S. Inoue, H. Koinuma and T. J. Tsuruta, *Polym. Sci., Part B: Polym. Lett.*, 1969, **7**, 287.

3 (a) X.-B. Lu, W.-M. Ren and G.-P. Wu, *Acc. Chem. Res.*, 2012, **45**, 1721; (b) G. Trott, P. Saini and C. Williams, *Philos. Trans. R. Soc., A*, 2016, **374**, 20150085; (c) S. Poland and D. J. Darensbourg, *Green Chem.*, 2017, **19**, 4990; (d) X. Zhang, M. Fevre, G. O. Jones and R. M. Waymouth, *Chem. Rev.*, 2018, **118**, 839; (e) C. M. Kozak, K. Ambrose and T. S. Anderson, *Coord. Chem. Rev.*, 2018, **376**, 565; (f) A. J. Plajer and C. K. Williams, *Angew. Chem., Int. Ed.*, 2022, **61**, e202104495; (g) C. A. L. Lidston, S. M. Severson, B. A. Abel and G. W. Coates, *ACS Catal.*, 2022, **12**, 11037.

4 S. Kissling, M. W. Lehenmeier, P. T. Altenbuchner, A. Kronast, M. Reiter, P. Deglmann, U. B. Seemann and B. Rieger, *Chem. Commun.*, 2015, **51**, 4579.

5 A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212.

6 T. Ohkawara, K. Suzuki, K. Nakano, S. Mori and K. Nozaki, *J. Am. Chem. Soc.*, 2014, **136**, 10728.

7 (a) J. Herzberger, K. Niederer, H. Pohlit, J. Seiwert, M. Worm, F. R. Wurm and H. Frey, *Chem. Rev.*, 2016, **116**, 2170; (b) Y. Xia, J. Shen, H. Alamri, N. Hadjichristidis, J. Zhao, Y. Wang and G. Zhang, *Biomacromolecules*, 2017, **18**, 3233; (c) X. Wang, Y. Liu, Z. Li, H. Wang, H. Gebru, S. Chen, H. Zhu, F. Wei and K. Guo, *ACS Macro Lett.*, 2017, **6**, 1331; (d) S. Liu, C. Ren, N. Zhao, Y. Shen and Z. Li, *Macromol. Chem. Phys.*, 2018, **39**, 1800485; (e) J. Shi, Z. Liu, N. Zhao, S. Liu and Z. Li, *Macromolecules*, 2022, **55**, 2844.

8 (a) K. Issleib and M. Lischewski, *Synth. Inorg. Met.-Org. Chem.*, 1973, **3**, 255; (b) P. Haasemann and J. Goubeau, *Z. Anorg. Allg. Chem.*, 1974, **408**, 293; (c) H. Goldwhite, P. Gysegem, S. Schow and C. Swyke, *J. Chem. Soc., Dalton Trans.*, 1975, 12; (d) R. Appel and M. Halstenberg, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 263.

9 (a) A. P. Dove, *ACS Macro Lett.*, 2012, **1**, 1409; (b) C. G. Jaffredo, J.-F. Carpentier and S. M. Guillaume, *Macromol. Rapid Commun.*, 2012, **33**, 1938; (c) M. J. Ji, M. Q. Wu, J. Y. Han, F. J. Zhang, H. W. Peng and L. H. Guo, *Curr. Org. Chem.*, 2021, **25**, 272.

10 (a) H. Zhang, S. Hu, J. Zhao and G. Zhang, *Macromolecules*, 2017, **50**, 4198; (b) H. Li, J. Zhao and G. Zhang, *ACS Macro Lett.*, 2017, **6**, 1094.

11 D. Zhang, S. K. Boopathi, N. Hadjichristidis, Y. Gnanou and X. Feng, *J. Am. Chem. Soc.*, 2016, **138**, 11117.

12 (a) S. Y. Hu, G. X. Dai, J. P. Zhao and G. Z. Zhang, *Macromolecules*, 2016, **42**, 4462; (b) H. X. Zhang, S. Y. Hu, J. P. Zhao and G. Z. Zhang, *Macromolecules*, 2017, **50**, 4198; (c) H. X. Zhang, S. Y. Hu, J. P. Zhao and G. Z. Zhang, *Eur. Polym. J.*, 2017, **95**, 693.

13 J. Zhang, L. Wang, S. Liu and Z. Li, *Angew. Chem., Int. Ed.*, 2021, **61**, e212111197.

14 P. C. B. Widger, S. M. Ahmed and G. W. Coates, *Macromolecules*, 2011, **44**, 5666.

15 P. Biagini, R. Po, S. Losio and M. Brivio, WO2020229965A1, 2020.

16 H. Sugimoto and K. Kuroda, *Macromolecules*, 2008, **41**, 312.

17 W. Xia, *PhD thesis*, Technische Universität München, 2015, https://d-nb.info/1071370049/34.

18 D. J. Darensbourg, R. M. Mackiewicz, J. L. Rodgers, C. C. Fang, D. R. Billodeaux and J. H. Reibenspies, *Inorg. Chem.*, 2004, **43**, 6024.

19 J. L. Leighton and E. N. Jacobsen, *J. Org. Chem.*, 1996, **61**, 389.

20 C. E. Anderson, S. I. Vagin, W. Xia, H. Jin and B. Rieger, *Macromolecules*, 2012, **45**, 6840.

21 K. D. Demadis, T. J. Meyer and P. S. White, *Inorg. Chem.*, 1998, **37**, 3610.

22 (a) L. Veronese, M. Brivio, P. Biagini, R. Po, I. Tritto, S. Losio and L. Boggioni, *Organometallics*, 2020, **39**, 2653; (b) P. Biagini, C. Perego, R. Po, L. Boggioni, M. Cozzolino, S. Losio, A. Flamigni, A. Colombo, C. Dragonetti, F. Fagnani, P. Matozzo and D. Roberto, *Inorg. Chim. Acta*, 2022, **532**, 120753.

23 H. Sugimoto, H. Otsuka and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 4172.

24 K. Nakano, M. Nakamura and K. Nozaki, *Macromolecules*, 2009, **42**, 6972.

25 G. Wu, S. Jiang, X. Lu, W. Ren and S. Yan, *Chin. J. Polym. Sci.*, 2012, **30**, 487.

26 E. N. Jacobsen, M. Tokunaga and J. F. Larrow, *PCT Int. Appl*, WO 00/09463, 2000.

27 B. Li, R. Zhang and X.-B. Lu, *Macromolecules*, 2007, **40**, 2303.

28 (a) B. O. Li, G. P. Wu, W. M. Ren, Y. M. Wang, D. Y. Rao and B. X. Lu, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6102; (b) K. Nozaki, K. Nakano and T. Hiyama, *J. Am. Chem. Soc.*, 1999, **121**, 11008; (c) M. Cheng, N. A. Darling, E. B. Lobkovsky and G. W. Coates, *Chem. Commun.*, 2000, 2007; (d) C. T. Cohen, C. M. Thomas, K. L. Peretti, E. B. Lobkovsky and G. W. Coates, *Dalton Trans.*, 2006, 237.

29 (a) D. J. Darensbourg and A. L. Phelps, *Inorg. Chem.*, 2005, **44**, 4622; (b) A. Decortes, A. M. Castilla and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2010, **49**, 9822.

30 D. J. Darensbourg;, R. M. Mackiewicz;, J. L. Rodgers and A. L. Phelps, *Inorg. Chem.*, 2004, **43**, 1831.

31 Y. Qin, X. Wang, S. Zhang, X. Zhao and F. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 5959.

32 H. Sugimoto, T. Aida and S. Inoue, *Macromolecules*, 1990, **23**, 2869.

33 D. J. Darensbourg and R. M. Mackiewicz, *J. Am. Chem. Soc.*, 2005, **127**, 14026.

34 C. T. Cohen and G. W. Coates, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 5182.

35 As suggested by reviewers, one case, at least, of the MALDI-ToF-MASS spectrum should be present and discussed in this work.

36 S. Penczek, M. Cypryk, A. Duda, P. Kubisa and S. Słomkowski, *Prog. Polym. Sci.*, 2007, **32**, 247.