

Effect of Quaternary Phosphonium Salts as Cocatalysts on Epoxide/ CO_2 Copolymerization Catalyzed by salen-Type Cr(III) Complexes

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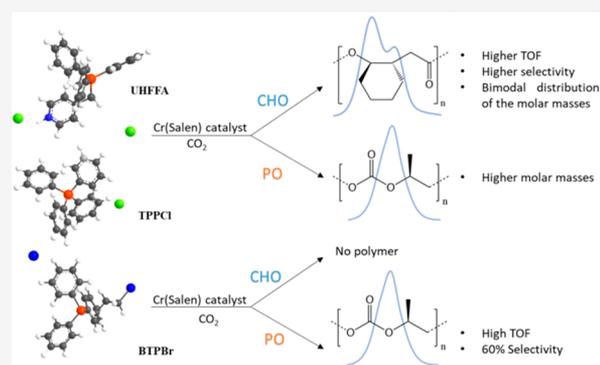
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ABSTRACT: Organic quaternary phosphonium salts are used in conjunction with chromium salen complexes in the alternating copolymerization of CO_2 and cyclohexene oxide (CHO) or propylene oxide (PO). A highly efficient formation of atactic polycarbonate with narrow distribution and molecular weights comparable or superior to those obtained with bis(triphenylphosphine)iminium (PPN^+) salts can be achieved with phosphonium salts such as triphenyl(4-pyridinylmethyl)phosphonium chloride hydrochloride (UHFFA) and tetraphenylphosphonium chloride (TPPCL). For CHO-based copolymers, a structure–property correlation can be observed: the T_g value seems to be related both to the amount of ether linkages and to the molecular weight. In addition, in the case of CHO, FTIR/ATR spectroscopy on the *pretreated* catalytic system can reliably predict the success of the copolymerization before the introduction of the epoxide monomer. Equilibria between the cation and anion in the phosphonium salts under study and the competition between epoxide and X^- have been shown to play a role in the activity, molecular weight, selectivity, and polymer properties. A general view of these equilibria and of the polymerization mechanism has been given as well as a rationale of differences in CHO and PO copolymerization behavior and polymer properties.



INTRODUCTION

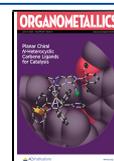
The reuse of carbon dioxide has attracted much attention in recent years thanks to the economic and environmental benefits deriving from the use of renewable sources and the growing concern about the greenhouse effect.¹ In particular, the catalytic transformation of CO_2 into biodegradable polycarbonates by alternating copolymerization with epoxides appears to be of great interest among both academic and industrial researchers.^{2–6} The first explorations of catalytic systems for the synthesis of polycarbonates date back to 1969, when Inoue et al. provided the first indications regarding the reactions between carbon dioxide and epoxides, mediated by a zinc derivative such as ZnEt_2 .⁷ The first reactions carried out with propylene oxide (PO) showed low reactivity of the catalytic systems and inconsistent carbonate contents.

After this pioneering work, the research of a proper catalyst for the reaction between carbon dioxide and epoxides continued for many years and, in the last few decades, a wide range of organometallic catalysts based on different metals have been synthesized. Although zinc has long been the metal of choice for designing both heterogeneous and homogeneous catalysts,^{8,9} other metal catalysts (mainly cobalt, chromium, and aluminum) have been exploited for this

reaction.^{10–17} It soon became clear that the catalytic activity of these complexes was significantly enhanced in the presence of a nucleophilic cocatalyst. Since then, much attention has been directed to discovering more efficient catalysts for these reactions and defining the best stoichiometric ratios among monomers, catalyst, and cocatalyst. The vast majority of the literature has been focused on catalyst structure modification, kinetic studies, or molar ratios between monomers and the catalytic system, almost always using well-known cocatalysts.^{17–20} In general, anions derived from PPN^+X^- ($\text{PPN}^+ = (\text{Ph}_3\text{P})_2\text{N}^+$ and $\text{X}^- = \text{halide, azide, acetate, nitrate, dinitrophenolate}$) salts are universally regarded as the most versatile and active cocatalysts.^{21–23} Aromatic Lewis bases, such as DMAP and *N*-methylimidazole, are also widely used, although they give activities much lower than those of the aforementioned

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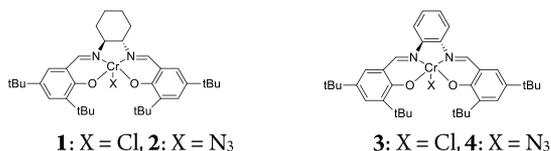
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cocatalysts. Only very few papers have focused on possible new families of cocatalysts.

The present study aims to investigate the effect of the structure of different quaternary phosphonium halides on the overall catalytic performances (i.e., catalyst activity, product selectivity, molecular weight, and molecular weight distribution) in the copolymerization of carbon dioxide with cyclohexene oxide (CHO) or propylene oxide (PO) using salen-type chromium complexes, the most common and studied catalysts (Chart 1).

Chart 1. Salen-Type Chromium Catalysts Used in This Work



The phosphonium salts considered as potential cocatalysts (shown in Chart 2) are halide salts (chlorides or bromides), with different degrees of nucleophilicity and polarizability. As shown from the general mechanism depicted in Scheme 1, the nucleophilicity of the cocatalyst may play a role in the selectivity and activity of the systems.

The substituents on the phosphorus(V) atom cover a vast range of aliphatic and aromatic moieties, exhibiting both electron-withdrawing (e.g., aldehydes, carboxylic acids) and electron-donating (alkyl chain arms, heterocycles) groups.

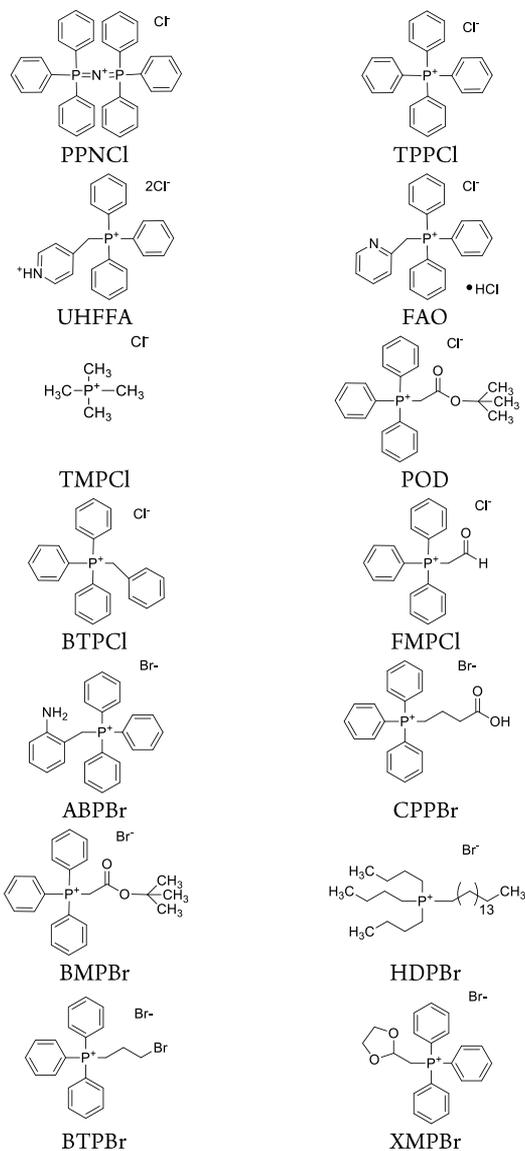
Initially, a screening among all cocatalysts was carried out and, once the most active compounds were identified, the temperature, CO₂ pressure, reaction time, and catalyst to cocatalyst and catalyst to monomer ratios were varied to obtain the best reaction conditions to achieve high monomer conversion, copolymer selectivity, and molecular weight.

Relevance has been given to the resulting properties of the polycarbonates obtained. We propose a correlation between the cocatalyst nature (nucleophilic anion, electronegativity, cationic steric hindrance, and interaction with the anion) and the features of the synthesized copolymers. Finally, a pretreatment between catalyst and cocatalyst made possible an analysis, via infrared spectroscopy, of the formation of the catalytically active species, which proved to be decisive for the purpose of the reaction.

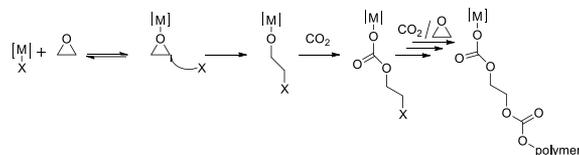
RESULTS AND DISCUSSION

This work is focused on an investigation of the quaternary phosphonium salt family as cocatalysts in the alternating copolymerization of carbon dioxide with epoxides. Two epoxides, CHO and PO, were used to make a comparison at a chemical level and to assess if an influence of the cation on the final polymeric material exists. Despite their great variety and commercial availability, only a few examples of tetrahedral quaternary phosphonium salts used in the copolymerization of epoxides with either anhydrides or CO₂ are found in the literature.^{23,24} The phosphonium salts considered as potential cocatalysts in this study (Chart 2) are chloride or bromide salts, with different degrees of nucleophilicity and polarizability. The substituents on the phosphorus(V) atom are aliphatic or aromatic moieties, with electron-withdrawing and electron-donating groups. All of the reactions were carried out

Chart 2. Quaternary Onium Chlorides (First, Second, Third, and Fourth Rows) and Bromides (Fifth, Sixth, and Seventh Rows) Tested As Cocatalysts (PPNCl as Reference)



Scheme 1. Mechanism for Polycarbonate Formation



in the presence of the well-known salen-type chromium catalysts shown in Chart 1 after pretreatment between the catalyst and cocatalyst.

Copolymerization of CO₂ and Cyclohexene Oxide (CHO). In the copolymerization of cyclohexene oxide with CO₂, all of the phosphonium salts shown in Chart 2 have been tested as cocatalysts with catalyst 1. All of the reactions were carried out in neat epoxide at 80 °C for 3.5 h. A pretreatment of the catalyst with the cocatalyst was always carried out to ensure maximum catalytic activity, by dissolving them in dry dichloromethane followed by vacuum removal of the solvent.

Table 1. Copolymerization Reaction of CHO and CO₂ with Catalyst 1 and Different Cocatalysts^a

entry	cocatalyst	P (bar)	conversion ^b (%)	sel ^b (%)	ether linkage ^b (%)	TOF ^c	M _n ^d (g/mol)	PDI ^d	T _g ^e (°C)
1 ^f	PPNCl	30 _{batch}	<0.1						
2	PPNCl	30 _{batch}	65	>99		465	13300	1.15	119
3	PPNCl	30 _{flow}	64	>99		450	10700	1.14	119
4	UHFFA	30 _{batch}	59	>99	<1	428	13600	1.10	118
5	UHFFA	30 _{flow}	49	>99	2	351	7000	1.26	116
6	TPPCL	30 _{batch}	35	>99	4	250	9200	1.09	112
7	TPPCL	30 _{flow}	21	>99	<1	152	4200	1.30	112
8	FAO	30 _{batch}	4	91	30	27	6400	2.82	62
9	FAO	30 _{flow}	3	96	16	23	9100	2.13	66

^aReaction conditions unless specified otherwise: [Cat]:[Cocat]:[CHO] = 1:1:2500; T = 80 °C; batch, CO₂ is introduced at t = 0; flow, continuous flow of CO₂, t = 3.5 h. ^bDetermined by ¹H NMR spectroscopy. Conversion = moles of epoxide reacted; selectivity = moles of polymer over cyclic carbonate. ^cMoles of CHO consumed per mole of Cr per hour. ^dDetermined by SEC using a polystyrene standard. ^eDetermined from DSC second heating cycle. ^fNo catalyst, [Cat]:[Cocat]:[CHO] = 0:1:2500.

Two sets of reactions have been carried out and compared: in *batch* copolymerization reactions were carried out by pressurizing the autoclave to the desired pressure with CO₂, and in the *flow* copolymerization reactions the CO₂ pressure was kept constant during copolymerization by continuously introducing it into the autoclave during the whole reaction time. In the absence of the pretreatment step, the cocatalyst was insoluble in the reaction medium and only an opalescent liquid was obtained.

Selected results are compared with those obtained with the reference PPNCl, a commercially available onium salt with a bulky cation and a strongly nucleophilic anion, in Table 1. A copolymerization with PPNCl and in the absence of a catalyst has been performed to show the inactivity of the cocatalyst alone in the copolymerization of CHO with CO₂. Entries exhibiting low polymerization activity (conversions lower than 3%) under the evaluated reaction conditions are not shown in Table 1.

In general, batch reactions gave the best results, independent of the onium salt used in terms of conversion and molecular weight, except for FAO. This is probably due to the accumulation in the reaction medium of impurities contained in CO₂ gas.

Phosphonium bromides were discovered not to act as cocatalysts in the reactions of CHO with CO₂ under the present conditions. They did not lead to a polymer or a cyclic product, even though a nucleophile such as Br⁻, a good leaving group, could favor ring closure and lead to higher selectivities toward cyclic carbonate rather than to linear copolymers.²⁵

With regard to the quaternary onium chlorides, the bifunctional pyridinium/phosphonium dichloride salt UHFFA showed conversion and polymer molecular weight comparable to those of the reference PPNCl, while the TPPCL cocatalyst afforded a moderate conversion (35%) and lower molecular weight. When FAO, a structural isomer of the UHFFA salt, is used, a very low conversion is obtained, in contrast with the good catalytic activity of the former. Thus, a good catalytic activity can probably arise only from those cations which can effectively delocalize the positive charge, while the presence of polarized groups (aldehydes, esters) or alkyl electron-donating substituents (methyls) led to no catalytic effect, despite the efficacy of the Cl⁻ nucleophile. An explanation of the difference between UHFFA and FAO seems to arise from an IR characterization of UHFFA, which shows two bands at 3480 cm⁻¹ (ν_{asym}(NH⁺)) and 718 cm⁻¹ (ω(NH⁺)), ascribable to the presence of a pyridinium salt.²⁶

Since similar bands are not detected in the IR spectrum of FAO, we can assume that, in the case of the more hindered *o*-pyridine, the molecule is in a hydrochloride salt form. Indeed, the presence of a free HCl molecule in FAO might reasonably interfere in the copolymerization reaction, leading to a rapid decomposition of the catalytic system.

A selectivity higher than 99% of polycarbonate (PCHC) over cyclic carbonate (CHC) has been achieved with the two most promising cocatalysts UHFFA and TPPCL, with the signals attributable to *trans* cyclic carbonate hardly emerging from the baseline in the ¹H NMR spectra (Table 1, entry 4, reported in Figure 1). According to the FTIR analysis *cis*-CHC

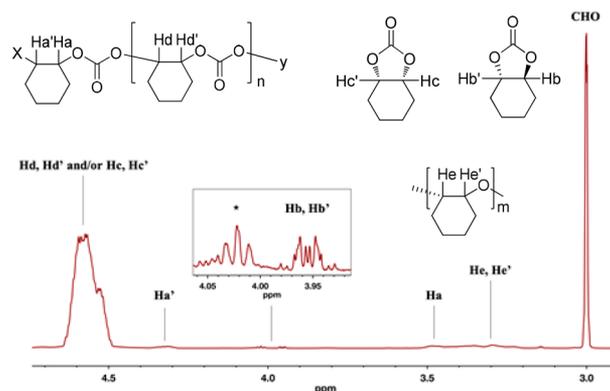


Figure 1. Selected region of the ¹H NMR spectrum of the crude poly(cyclohexene carbonate) (Table 1, entry 4). The methines at 3.05 ppm of the unreacted CHO are visible. Both *cis*-CHC and *trans*-CHC structures and related chemical shifts are indicated, though from FTIR analysis *cis*-CHC is not formed.

products are not formed during the reaction, as confirmed by the absence of the peak at 1804 cm⁻¹ typical of *cis*-CHC. The polymer samples were also analyzed by ¹³C NMR (Figure 2). As expected, the use of a nonstereospecific catalyst led to the formation of atactic polymers, with the *syndio* and *iso* signals each accounting for ca. 50% of the total signals.²⁷

The best results in terms of molecular weight have been achieved using UHFFA under batch conditions. The use of such a salt allowed for the synthesis of polymers characterized by a molecular weight of 13600 g/mol with very narrow polydispersity. In all of these cases, with both UHFFA and TPPCL, a bimodal distribution of the molecular weights was observed in the SEC curves, with the M_p value relative to the fraction at lower molecular weight almost always prevailing

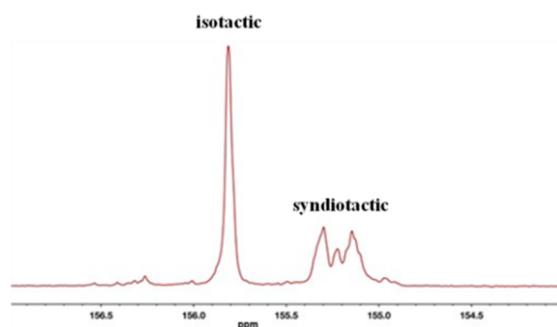


Figure 2. Region of the ^{13}C NMR spectrum of poly(cyclohexene carbonate) (Table 1, entry 4) in which the signals due to the C=O groups of the carbonate group appear.

over that of the high-molecular-weight fraction with a ca. 2:1 ratio (Figure 3).

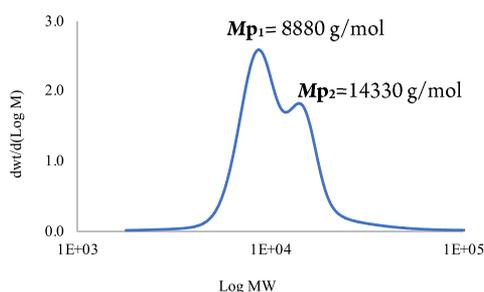


Figure 3. SEC bimodal curve of the obtained poly(cyclohexene carbonate) (Table 1, entry 6).

Such behavior is commonly observed for poly(cyclohexene carbonate) from salen-type catalysts. Darensbourg et al.²⁸ attributed this bimodality to the simultaneous growth of two polymeric chains on both sides of the MN_2O_2 plane. Alternatively, Nozaki¹⁷ and Sugimoto²⁹ proposed that this bimodality originated from chain transfer processes due to the presence of traces of contaminant water in the reaction mixture. This latter hypothesis has been confirmed by a recent study.³⁰ Moreover, it is worth noting that in our experiments the M_{p2} value is always almost double that of M_{p1} . This seems to be in line with what was found by Williams³¹ and successively Darensbourg,³² who demonstrated that trace amount of water reacts with CHO to produce cyclohexane-1,2-diol³³ which act as a chain-transfer agent. Cyclohexane-1,2-diol leads to a new initiating species (a diol) that can propagate from both of the hydroxyl end groups, giving chains with

approximately twice the M_n values in comparison to the chain lengths initiated from halides.

When FAO was used as a cocatalyst, a broader polydispersity along with a lower molecular weight in the case of Table 1, entries 8 and 9, was found, which might be justified by the occurrence of various chain-transfer mechanisms in the reaction, promoted by the presence of HCl in the reaction mixture.

The most promising phosphonium salt, UHFFA, characterized by a double phosphonium/pyridinium cation, has been studied under different CO_2 pressures and temperatures (Table 2) and CHO/cat and catalyst/cocatalyst ratios (Table 3) with catalyst 1 to identify the best reaction conditions in terms of conversion, molecular weight, and selectivity. Finally, under the best conditions, copolymerization reactions of CHO and CO_2 with catalysts 1–3 and UHFFA have been compared (Table 4).

At 10 bar of pressure under our conditions, no conversion of the epoxide is observed. It is clear that at such a pressure an efficient reactivity of CO_2 is not possible. It is also important to note that 1/UHFFA in the absence of CO_2 does not homopolymerize CHO to form a polyether. The best results in terms of CHO conversion, selectivity, and molecular weight of polycarbonates are obtained at 30 bar of CO_2 pressure and 80 °C. It can be reasonably speculated that, at higher CO_2 pressure in the reaction, the free CHO monomer competes less with CO_2 in the polymerization cycle, thus slowing down the propagation step and leading to lower conversions and lower molecular weight.

At 50 °C the conversion is limited to half that reached at 80 °C; as the temperature is increased, the catalytic performance improves. However, at 120 °C the conversion decreases with the formation of some cyclic carbonate, (4% vs none in all the other cases). Moreover, some polyether linkages are formed at high temperature.

The effects of monomer loading and catalyst to cocatalyst ratio were also investigated. As expected, the greater the amount of catalyst, the greater the TOF (e.g., entry 4 vs entry 14 and entry 16 vs entry 17), but some differences are encountered in the molecular weights (Table 3).

With regard to the catalyst to cocatalyst ratio, the phosphonium pyridinium chloride UHFFA is most effective in a 1:1 ratio with the metal complex. Interestingly, the low conversion value obtained with a 1:0.5 ratio suggests zero or very minor contribution of the second chloride to the ring opening, which allows us to consider UHFFA as a monoanionic cocatalyst.

An almost linear correlation can be drawn between the conversion values and the molecular weight obtained in these

Table 2. Effect of Pressure and Temperature on the Copolymerization Reaction of CHO and CO_2 by Cr(salen)Cl and UHFFA^a

entry	P (bar)	T (°C)	conversn ^b (%)	sel ^b (%)	ether linkage ^b (%)	TOF ^c	M_n^d (g/mol)	PDI ^d	T_g^e (°C)
10	10	80	0	0	0	0			
4	30	80	59	>99	<1	428	13600	1.10	118
11	40	80	44	>99	<1	314	9800	1.13	116
12	30	50	30	>99	<1	211	6200	1.21	112
13 ^f	30	120	42	96	4	300	7500	1.11	118

^aReaction conditions: [Cat]:[Cocat]:[CHO] = 1:1:2500; batch, CO_2 is introduced at $t = 0$, $t = 3.5$ h. ^bDetermined by ^1H NMR spectroscopy. Conversion = moles of epoxide reacted; selectivity = moles of polymer over cyclic carbonate. ^cMoles of CHO consumed per mole of Cr. ^dDetermined by SEC using a polystyrene standard. ^eDetermined from DSC second heating cycle. ^fFlow reaction.

Table 3. Effect of Molar Ratio between Catalyst and CHO on the Copolymerization Reaction of CHO and CO₂ by Cr(salen)Cl and UHFFA^a

entry	Cat (mmol)	Cat:CHO	Cat:Cocat	conversn ^b (%)	sel ^b (%)	ether linkage ^b (%)	TOF ^c	M _n ^d (g/mol)	PDI ^d	T _g ^e (°C)
14	0.04	1:1000	1:1	63	>99		180	10400	1.13	110
4	0.10	1:2500	1:1	60	>99	<1	428	13600	1.10	118
15	0.07	1:5000	1:1	32	>99	<1	457	7500	1.17	84
16	0.14	1:2500	1:0.5	42	>99	-	300	9500	1.13	73
17	0.04	1:2500	1:2	35	>99	<1	250	5300	1.23	99

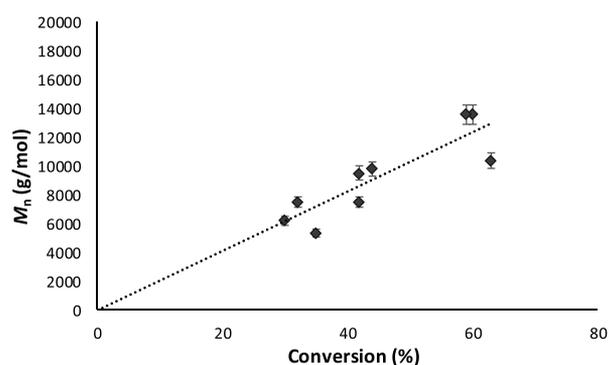
^aReaction conditions: $T = 80\text{ }^{\circ}\text{C}$; $P = 30\text{ bar}$; batch, CO₂ is introduced at $t = 0$, $t = 3.5\text{ h}$. ^bDetermined by ¹H NMR spectroscopy. Conversion = moles of epoxide reacted; selectivity = moles of polymer over cyclic carbonate. ^cMoles of CHO consumed per mole of Cr per hour. ^dDetermined by SEC using a polystyrene standard. ^eDetermined from DSC second heating cycle.

Table 4. Copolymerization Reaction of CHO and CO₂ with Catalysts 1–3 and UHFFA^a

entry	Cat	conversn ^b (%)	sel ^b (%)	ether linkage ^b (%)	TOF ^c	M _n ^d (g/mol)	PDI ^d	T _g ^e (°C)
17	1	60	>99	<1	428	13600	1.10	118
18	2	82	99	1	586	9100	1.13	119
19	3	44	97	2	317	5600	1.24	116

^aConditions: [Cat]:[Cocat]:[CHO] = 1:1:2500; $T = 80\text{ }^{\circ}\text{C}$; $P = 30\text{ bar}$; $t = 3.5\text{ h}$. ^bDetermined by ¹H NMR spectroscopy. ^cMoles of CHO consumed per moles of Cr per hour. ^dDetermined by SEC using a polystyrene standard. ^eDetermined from DSC second heating cycle.

conditions with UHFFA (Figure 4). It can be observed that the error increases with conversion.

**Figure 4.** Relationship between conversion and molecular weight with UHFFA as cocatalyst.

Additionally, the two salen-type catalysts 2 and 3, whose nucleophilic and imino groups had been respectively modified, were also tested with UHFFA (Table 4). Catalyst 2, the azido derivative of 1, afforded an improvement in the overall conversion and TOF of the copolymerization reaction, while the molecular weight slightly drops but remains of the same magnitude, as reported in the literature for Cr(salen)N₃/PPNCl systems.²⁸ The more electron poor backbone of catalyst 3 has instead a general detrimental effect on the polymerization performances, partially deactivating the nucleophilic group on the metal center by retaining the electronic density on the aromatic ring, resulting in a decrease in the polymerization rate.

By observation of the data reported in the previous tables, some differences in the glass transition temperature of the obtained copolymers appear. The highest values (110–120 °C) are in agreement with those previously reported for pure PCHC.³⁴ Lower T_g values are due to the presence of ether linkages above 15% or to lower molar mass.^{35,36}

Table 5. Copolymerization Reaction of PO and CO₂ with Catalyst 4 and Different Cocatalysts^a

entry	Cocat	conversn ^b (%)	sel ^b (%)	ether linkage ^b (%)	TOF ^c	M _n ^d (g/mol)	PDI ^d	T _g ^e (°C)
1	PPNCl	73	64	10	75	26000	1.29	34
2	TPPCL	83	90	5	86	25700	1.14	39
3	UHFFA	84	64	11	87	21700	1.23	35
4	FAO	59	68	16	61	18200	1.07	30
5	BTPCL	39	45	19		12500	1.07	26
6	TMPCl	25	85	10		nd ^f	nd	30
7	POD	7	35	46	7			no precipitate obtained
8	FMPCl	28	87	15		nd	nd	20
9	BTPBr	60	58	3	62	12800	1.13	36
10	HDPBr	54	83	9	56	nd	nd	38
11	XMPBr	31	52	33	32	nd	nd	nd
12	ABPBr	10	26	43	10			no precipitate obtained
13	BMPBr	11	53	37	11			no precipitate obtained
14	CPPBr	20	27	38	21			no precipitate obtained

^aReaction conditions: [Cat]:[Cocat]:[PO] = 1:0.5:2500; $T = 60\text{ }^{\circ}\text{C}$; $P = 30\text{ bar}$; $t = 24\text{ h}$. ^bDetermined by ¹H NMR spectroscopy. Conversion = moles of epoxide reacted; selectivity = moles of polymer over cyclic carbonate. ^cMoles of PO consumed per mole of Cr per hour. ^dDetermined by SEC using a polystyrene standard. ^eDetermined from DSC second heating cycle. ^fnd = not determined.

Copolymerization of CO₂ and Propylene Oxide (PO).

The electronic effect of the salen-type skeleton strongly affects the copolymerization results according to the monomer used. Indeed, while electron-rich diimine backbones (cyclohexyl ring) are highly effective with cyclohexene oxide, their use with propylene oxide mostly leads to the formation of cyclic carbonate.^{37,38} In contrast, thanks to its electron-poor aromatic ring, catalyst **4** affords the best selectivity toward poly(propylene carbonate) (PPC). Thus, we have selected catalyst **4** for the study of all the cocatalysts shown in Chart 2. The results are collected in Table 5.

All of the copolymerizations involving propylene oxide were carried out in neat epoxide at 60 °C following the batch procedure described in the CHO copolymerization section. As in the case of CHO, pretreatment of the catalytic system was always carried out. A catalyst to cocatalyst ratio of 1:0.5 has been used here to afford the best polymerization rate, as reported in the literature.³⁷ Given the higher activation energy required to produce poly(propylene carbonate) in comparison to poly(cyclohexene carbonate), 67.6 kJ vs 46.9 kJ, the reaction time was increased to 24 h.^{37,38} All of the cocatalysts investigated in this work exhibit catalytic activity with PO, although the conversion and selectivity differ to a great extent (Table 5). From the data presented in Table 5, phosphonium salts whose cations are more able to delocalize positive charge show improved activity in the copolymerization reaction.

Selectivity values, calculated as moles of polymer over cyclic carbonate, vary considerably, and generally cocatalysts showing low activities also have low selectivity. Moreover, a certain percentage of polyether is always obtained in all of the polymeric samples prepared, as revealed by the ¹H NMR peak at 3.5 ppm (Figure 5). It must be noted that, if the conversion

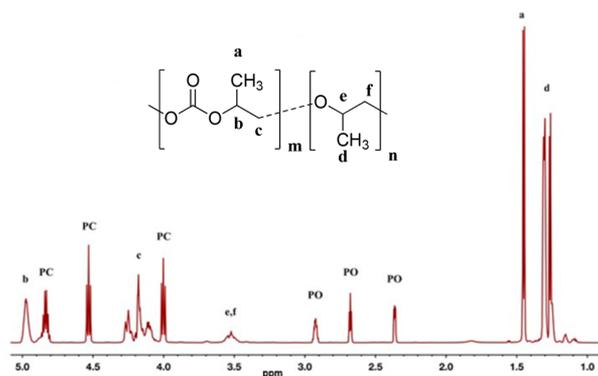


Figure 5. ¹H NMR spectrum of crude poly(propylene carbonate) (Table 5, entry 14). Cyclic propylene carbonate (PC) and unreacted PO signals are visible.

does not exceed 20%, no solid product can be collected through precipitation. As is widely known, the use of a symmetric, nonstereospecific salen-type catalyst does not allow stereoselectivity, and all of the possible stereosequences (iso-, syndio-, and atactic) of the HT regiosequence are present together.⁹ Moreover, the three possible regiosequences, head to tail (HT), head to head (HH), and tail to tail (TT), for PPC appear in the ¹³C NMR spectrum (Figure 6).

The best conversions in the copolymerization reactions of PO and CO₂ are obtained with UHFFA and TPPCl, as in CHO copolymerization. In particular, tetraphenylphosphonium chloride afforded the best results among all the cocatalysts in terms of selectivity, exceeding the values

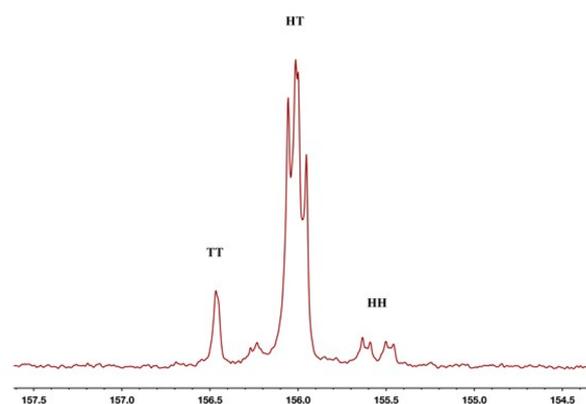


Figure 6. ¹³C NMR spectrum of poly(propylene carbonate) (Table 5, entry 14), in which the signals due to the C=O groups of the carbonate group appear.

obtained with the reference PPNCl cocatalyst. Also, the molecular weights were comparable (25700 g/mol vs 26000 g/mol, respectively).

The UHFFA salt afforded the same conversion of TPPCl but considerably lower selectivity (64%) and a higher amount of ether linkages. Polydispersity indexes indicate very narrow molecular weight distributions, and SEC curves can be regarded as essentially monomodal in all of the cases considered (Figure 7). A different behavior of FAO as a

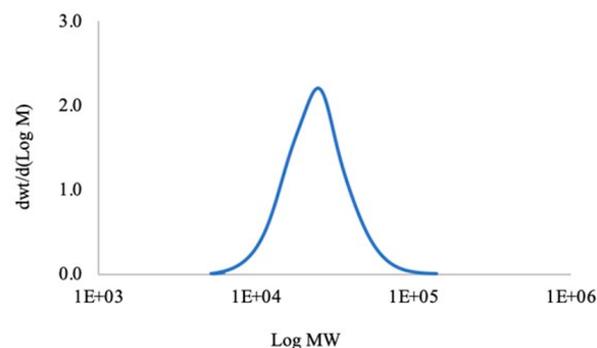


Figure 7. SEC monomodal curve of obtained poly(propylene carbonate) (Table 5, entry 2).

cocatalyst for propylene oxide has been observed in comparison to cyclohexene oxide. A very narrow PDI and a molecular weight not inferior to those obtained with other cocatalysts were achieved, allowing us to suppose that the free HCl molecule did not play a detrimental role in this case. The values of glass transition temperatures of poly(propylene carbonate) remain stable around 35 °C, as in the commercial PPC.

The highest and lowest *T_g* values are those of copolymers with the lowest and highest ether contents, respectively.

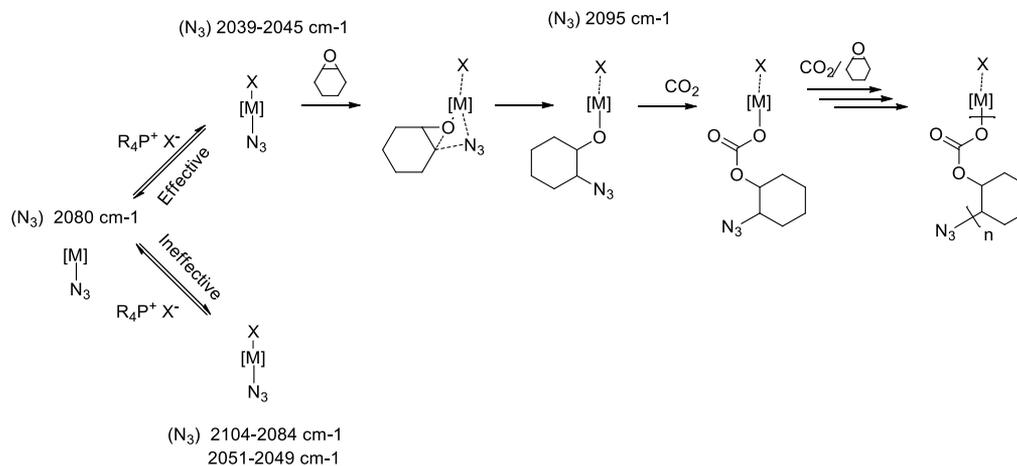
On the basis of the satisfying results obtained with UHFFA and TPPCl, the same polymerization tests have been conducted at 13 bar (Table 6). Neutral Lewis bases such as 4-dimethylaminopyridine (DMAP) have been shown to be more effective when they are used at pressures lower than those for PPNX salts;^{39,40} therefore, we have decided to use it as a reference cocatalyst in addition to PPNCl for this pressure.

As shown in Table 6, at lower CO₂ pressure for both of the phosphonium salts tested, UHFFA and TPPCl, a moderate

Table 6. Copolymerization Reaction of PO and CO₂ with Catalyst 4 and Different Cocatalysts^a

entry	Cocat	conversion ^b (%)	sel ^b (%)	ether linkage ^b (%)	TOF ^c	M _n ^d (g/mol)	PDI ^d	T _g ^e (°C)
15	PPNCl	50	86	1	52	21700	1.07	33
16	DMAP	60	90	1	62	12900	1.07	33
17	UHFFA	78	80	9	80	25300	1.27	36
18	TPPCL	71	74	7	74	24200	1.18	34

^aReaction conditions: [Cat]:[Cocat]:[PO] = 1:0.5:2500; P = 13 bar; T = 60 °C; t = 24 h. ^bDetermined by ¹H NMR spectroscopy. Conversion = moles of epoxide reacted; selectivity = moles of polymer over cyclic carbonate. ^cMoles of PO consumed per mole of Cr per hour. ^dDetermined by SEC using a polystyrene standard. ^eDetermined from DSC second heating cycle.

Scheme 2. Proposed Catalyst–Cocatalyst Interaction and CHO/CO₂ Polymerization Initiation Mechanism via Observed $\nu(\text{N}_3)$ 

decrease in the conversion can be observed, while entry 16 confirms how the best catalytic performances of DMAP are to be found under milder conditions.

While for PPNCl and UHFFA, the selectivity sensibly increases at low pressure moving from 64 to 86 mol % and from 64 to 80 mol %, respectively, the opposite result is observed with TPPCL. The percentage of etheral bonds seems to be unaffected by the pressure used; in all cases the value remains below 10%. Molecular weights of the obtained copolymers are, with all phosphonium salts, very similar to those obtained at 30 bar of CO₂, and the polydispersity indexes do not show significant variations.

FT-IR Study of the Catalytic System. FTIR spectroscopy has been shown by Darensbourg et al.⁴¹ to give interesting information on catalytic systems used in CHO/CO₂ copolymerization. The change in asymmetric stretching vibration of the coordinated azide in the Cr(salen)N₃ catalyst is a useful tool for understanding how the activation of the catalyst and the initiation of the polymer chain occur (for example, $\nu(\text{N}_3)$ 2080 cm⁻¹ in a noncoordinating solvent, also $\nu(\text{N}_3)$ 2053 cm⁻¹ in the solid state or a strongly coordinating solvent).⁴¹ The geometry of the metal center thus switches from pentacoordinate square pyramidal to a hexacoordinate octahedron.^{42,43} We attempted to elucidate the interactions between quaternary phosphonium P⁺X⁻ ionic cocatalysts and the catalyst prior to CHO/CO₂ copolymerization via FTIR. Indeed, the pretreatment of catalyst and cocatalyst allows for the fast activation of the catalytic system. We observed that the stretching vibration of the azide group shifts to lower values between 2039 and 2045 cm⁻¹ depending on the chemical nature of the anion, due to the trans effect of the coordinated X⁻ anion. Thus, fast coordination of the cocatalyst anion on

the free apical position of the chromium complex occurs. The hexacoordinate complex formed can be regarded as the real initiator of the copolymerization: the nucleophile opens an epoxide ring, thus moving from its position on the metal center to the terminal position on the new alkoxide ligand. This hypothesis is confirmed by the shift of the stretching vibration to 2095 cm⁻¹ after addition of CHO. This vibration is representative of the ring-opened organic azide derivative (whereas the stretching of free organic azides can be found around $\nu(\text{N}_3)$ 2120 cm⁻¹),⁴³ followed by a kinetically favored CO₂ insertion (see Scheme 2).

Among all the quaternary phosphonium salts tested in the present work, only those which are actually able to catalyze the production of PCHC show this feature, while all of the cocatalysts which revealed themselves ineffective in the CHO/CO₂ copolymerization exhibit a different behavior (Figure 8 and Table 7).

The pretreatment between the chromium complex and the onium salt does not lead to the observation by FTIR of a hexacoordinated species, even after several hours of stirring, suggesting a stronger interaction between the cation and anion. In fact, $\nu(\text{N}_3)$ remains at around 2080 cm⁻¹, representative of a five-coordinated complex, or sometimes shifts to higher values (around 2100 cm⁻¹), suggesting a partial electronic donation from N₃ to P⁺. With all cocatalysts, after addition of CHO, a stretching vibration at 2095 cm⁻¹ appears; this vibration is representative of the ring-opened organic azide derivative (see Scheme 2).

When the more electron poor salaphen catalyst 4 was pretreated with all the cocatalysts shown in Table 5, the IR spectra showed the same features. In fact, we found $\nu(\text{N}_3)$ at around 2050 cm⁻¹, for the pretreatments carried out with

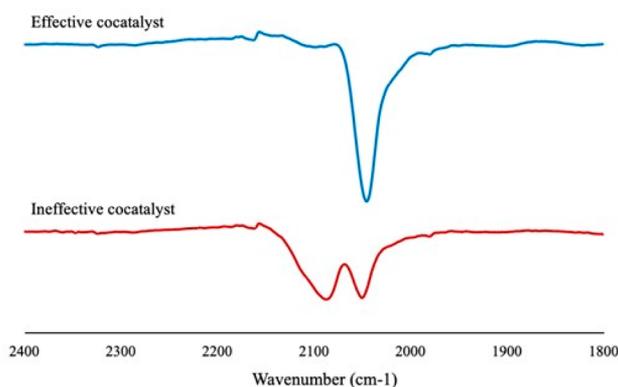


Figure 8. IR vibrations of coordinated N_3 after catalyst/cocatalyst pretreatment.

Table 7. IR Coordinated Azide Vibrations in Activated Catalytic Systems and Consequent Production of PCHC^a

Cocat	$\nu(N_3)$ (cm^{-1}) after pretreatment	$\nu(N_3)$ (cm^{-1}) in CHO	PCHC production
PPNCl	2039	2095	
UHFFA	2044	2095	
TPPCL	2045	2095	
FAO	not detectable ^b	not detectable ^b	
TMPCl	2099, 2050	2095	X
FMPCl	2088, 2051	2095	X
POD	2088, 2049	2095	X
ABPBr	2088, 2050	2095	X
CPPBr	2086, 2050	2095	X
BMPBr	2087, 2051	2095	X
HDPBr	2104, 2050	2095	X
BTPBr	2088, 2050	2095	X
XMPBr	2084, 2049	2095	X

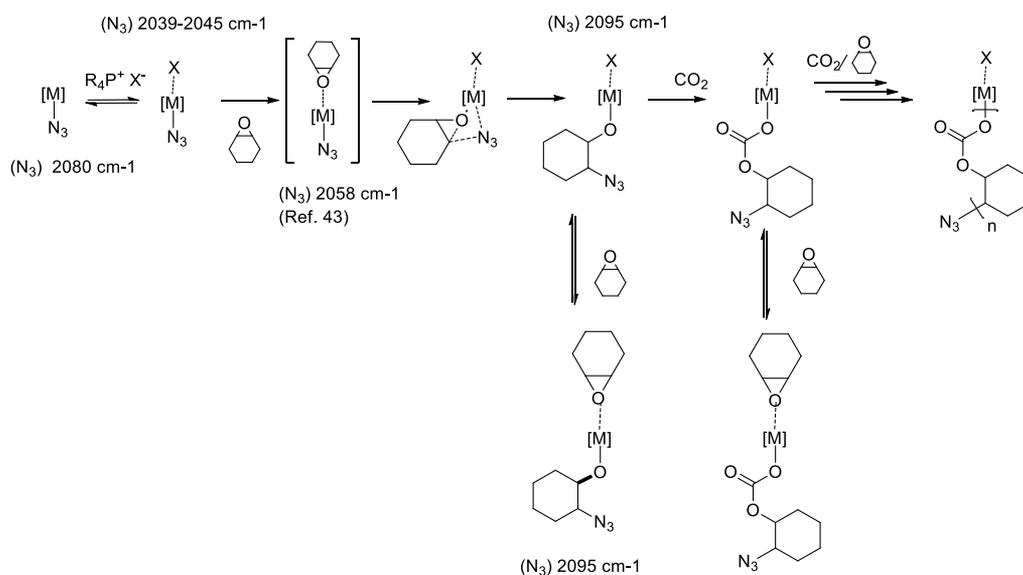
^aCat = Cr(salen) N_3 . ^bPresumably due to N_3 -HCl interaction.

PPNCl, UHFFA and TPPCL, while in all the other cases $\nu(N_3)$ was detected at around 2100 cm^{-1} . Nonetheless, contrary to

has been observed for cyclohexene oxide, all of the catalytic systems gave rise to the production of poly(propylene carbonate).

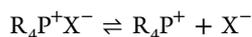
General Mechanistic Considerations. Marked differences in the catalytic behavior of propylene oxide and cyclohexene oxide have been observed: activities of CHO copolymerization greater than those of PO copolymerization, lower molar mass and bimodal distribution of the molecular weights in CHO copolymers, and catalyst/cocatalyst combinations that are not active in CHO copolymerization being efficacious in PO polymerization. Moreover, in an FTIR study we observe an apparent unpredictability in PO copolymerization and the presence of the same vibration at 2095 cm^{-1} after addition of CHO with both effective and ineffective cocatalysts. The greater activity and selectivity in CHO copolymerization can be explained by the kinetic studies by Darensbourg:^{37,44} CHO copolymerization has a lower activation barrier with respect to PO copolymerization, 46.9 kJ with respect to 67.6 kJ, and in contrast, higher activation barriers for cyclic carbonate formation of 133.0 and 100.5 kJ, respectively. The final ΔH_f values between copolymer and cyclic formation are -34 (CHO) and -54 (PO) kJ. However, it is counterintuitive to understand why PO copolymers reach higher molar masses with narrower molar mass distributions in comparison CHO copolymers, even though the TOF values of PO copolymerization are lower than those of CHO copolymerization. We hypothesized that CHO is more prone to chain-transfer processes in comparison to PO. During our studies a confirmation of this hypothesis derived from a recent study by Feng and Hadjichristidis, who reported that CHO and PO copolymerization with CO_2 can reach similarly high molar masses and monodisperse GPC curves under very accurate drying of CO_2 .³⁰ As far as the effect of the structure of different quaternary phosphonium halides on the overall catalytic performances in CHO and PO copolymerization with CO_2 is concerned, we note that most effective cocatalysts in CHO copolymerization are also the best in PO copolymerization. Those less effective in PO copolymerization give lower selectivity and/or higher ether linkages in the

Scheme 3. Proposed Catalyst–Cocatalyst Interaction and CHO/ CO_2 Polymerization Initiation Mechanism, Where the Role of Epoxide Coordination Is Evidenced



copolymers, and thus this indicates that with less effective cocatalysts the species spend more time in resting states. Collateral reactions, such as cyclic carbonate and ether linkage formation, which arise from metal carbonate and metal alcoxide intermediates,^{45,46} respectively, are more probable.

A rationale for the above results and for the apparent discrepancies, such as the unpredictability of FTIR study in PO copolymerization and the presence of the same vibration after addition of CHO in both effective and ineffective cocatalysts, can be found only if we consider as very important the interactions between the cation and anion in the following equilibrium:



The equilibrium shifts more to the right according to the basicity order $Cl^- > Br^- > I^-$ and the R_4P^+ ability to delocalize the positive charge. Halide basicity explains why bromides are less effective as cocatalysts.

The onium ability to delocalize the positive charge explains the FTIR shift at 2039–2045 cm^{-1} of the coordinated azide in activated catalytic systems given by the best cocatalysts, PPNCl, UHFFA, and TPPCl.

When the equilibrium shifts more to the left, we do not observe the active species with a vibration at 2039–2045 cm^{-1} . Nevertheless, these cocatalysts are active in PO copolymerization. We propose that all of the active species shown in Scheme 2 are in equilibrium with epoxide coordinated species, which can be considered as a resting state (see Scheme 3).⁴⁷ The lower coordination ability of PO with respect to CHO may shift these equilibria more toward the active species rather than to epoxide coordinated species, and this allows these cocatalysts to be effective, though with lower activities.

CONCLUSION

The use of quaternary phosphonium halide salts (chlorides or bromides), with different degrees of nucleophilicity and polarizability, as cocatalysts in CO_2 /epoxide copolymerization has been investigated here and compared to the use of the widely acknowledged PPNCl onium salt. The catalyst activity, product selectivity, molecular weight, and molecular weight distribution in the copolymerization of carbon dioxide with CHO or PO using salen-type chromium complexes has been studied. Highly efficient syntheses of atactic polycarbonate with narrow distribution and molecular weights comparable or superior to those obtained with PPN^+Cl^- have been achieved with phosphonium salts such as triphenyl(4-pyridinylmethyl)phosphonium chloride hydrochloride (UHFFA) and tetraphenylphosphonium chloride (TPPCL). In particular, the use of the mixed phosphonium/pyridinium UHFFA salt triphenyl(4-pyridinylmethyl)phosphonium chloride hydrochloride affords comparable conversions and molecular weights in the case of propylene oxide as a monomer. T_g values seem to be influenced by both the amount of ether linkages and molecular weight. Moreover, the IR monitoring of the premixing of the catalytic system prior to the actual copolymerization, using a N_3 derivative of the desired catalyst, affords in principle a reliable prediction of whether the reaction will actually produce polycarbonate or not. This can be achieved by simply evaluating the number and position of the $\nu(N_3)$ stretching vibrations on the activated catalyst. This prediction is useful when CHO is used as a monomer. Apparently, no prediction can be made for the PO/ CO_2 copolymerization. However, the

results are instructive because they give us information on the importance of the equilibria, which play a role in these polymerizations: that is, the equilibria between cation and anion in the phosphonium salts under study and the competition between epoxide and X^- . In conclusion, it has been possible to give a general view of these equilibria and of the polymerization mechanism and to give a rationale of the results obtained.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise specified, all of the 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 all of the phosphonium halides, were received from Sigma-Aldrich and used without further purification.

The phosphonium halides taken into account are bis-(triphenylphosphine)iminium chloride (PPNCl), tetraphenylphosphonium chloride (TPPCL), triphenyl(4-pyridinylmethyl)phosphonium chloride hydrochloride (UHFFA), triphenyl(2-pyridylmethyl)phosphonium chloride hydrochloride (FAO), tetramethylphosphonium chloride (TMPCL), tributylhexadecylphosphonium bromide (HDPBr), (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (XMPBr), (2-aminobenzyl)triphenylphosphonium bromide (ABPBr), (3-bromopropyl)triphenylphosphonium bromide (BTPBr), (formylmethyl)triphenylphosphonium chloride (FMPCL), (3-carboxypropyl)triphenylphosphonium bromide (CPPBr), (*tert*-butoxycarbonylmethyl)triphenylphosphonium bromide (BMPBr), (*tert*-butoxycarbonylmethyl)triphenylphosphonium chloride (POD), and Benzyltriphenylphosphonium chloride (BTPLC).

Dichloromethane, cyclohexene oxide, and propylene oxide were freshly distilled over CaH_2 . Carbon dioxide gas (99.999% purity) was purchased from Air Liquide. The deuterated solvent for NMR measurements (CD_2Cl_2) was used as received. Catalysts 2–4 (Chart 1) were synthesized according to the literature.^{23,48}

Synthesis of *N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)cyclohexenediimine Chromium(III) Azide (2). *N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)cyclohexenediimine chromium(III) chloride (1; 2 g, 3.16 mmol) was first dissolved in 250 mL of CH_3CN . Simultaneously, in another flask with a pressure-equalizing addition funnel, 1 equiv (0.66 g, 3.16 mmol) of $AgClO_4$ was dissolved in an equal volume of CH_3CN . The metal complex solution was transferred into the funnel and added dropwise over approximately 40 min. Immediate precipitation of $AgCl$ was observed, and the reaction was stirred overnight to ensure completion. The reaction mixture was then filtered into a flask already containing 3 equiv of NaN_3 , to minimize exposure to air. Sodium azide has a low solubility in CH_3CN ; thus the reaction mixture was stirred for another 24 h. The mixture was diluted with diethyl ether, the organic phase was washed with copious amounts of water to remove $NaClO_4$ and the unreacted excess of NaN_3 and then dried with $MgSO_4$, and the solvent was removed in vacuo, yielding a brown powder (1.78 g, 88% yield). ATR ν (cm^{-1}): 2949 (s), 2903 (m), 2864 (m), 2085 (s), 2057 (m), 1617 (s), 1530 (s), 1460 (m), 1434 (s), 1253 (s), 1198 (m), 1166 (s), 1026 (m), 871 (m), 835 (s), 784 (s), 746 (s), 561 (s), 541 (s). Anal. Calcd for $C_{36}H_{52}N_5O_2Cr$: C, 67.68; H, 8.20; N, 10.96. Found: C, 67.39; H, 8.77; N, 9.82.

Synthesis of *N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)phenylenediimine (SalaphenH₂). Benzene-1,2-diamine (2.0 g, 18.5 mmol), 3,5-di-*tert*-butylsalicylaldehyde (8.67 g, 37 mmol), and a few drops of aqueous formic acid were dissolved in 250 mL of methanol, heated to reflux for 3 h, and then cooled to room temperature. The product was isolated, washed with MeOH, dissolved in CH_2Cl_2 , washed again with a saturated NaCl solution, and then dried with $MgSO_4$. Evaporation of the solvent afforded a pale orange solid (6.0 g, 80% yield). 1H NMR (CD_2Cl_2 , 300 K, 500 MHz) δ_H (ppm): 8.71 (s, 2H), 7.47 (d, 2H), 7.37 (m, 2H), 7.28 (m, 4H), 7.31 (m, 4H), 1.44 (s, 18H), 1.33 (s, 18H).

Synthesis of *N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-phenylenediimine Chromium(III) Chloride (3). The SalaphenH₂ ligand (1.0 equiv, 4.0 g, 7.4 mmol) and chromium(II) chloride (1.1 eq, 1.0 g, 8.1 mmol) were dissolved in 350 mL of THF and stirred under nitrogen at ambient temperature for 24 h. The reaction mixture then was exposed to air and stirred for an additional 24 h. Diethyl ether was poured into the reaction mixture, and the organic layer was washed first with aqueous saturated NH₄Cl (3 × 200 mL) and then with brine (3 × 200 mL), followed by drying with MgSO₄. After filtration to remove solid impurities and drying agent, the solvent was removed under vacuum, yielding a dark red powder (4.5 g, 97% yield). ATR ν (cm⁻¹): 2951 (s), 2903 (m), 2866 (m), 1601 (s), 1577 (s), 1524 (s), 1482 (m), 1460 (m), 1425 (m), 1255 (s), 1195 (m), 1170 (s), 1133 (m), 1025 (m), 869 (m), 837 (m), 785 (m), 747 (s), 537 (s). Anal. Calcd for C₃₆H₄₆N₂O₂CrCl: C, 69.05; H, 7.40; N, 4.47. Found: C, 68.60; H, 8.06; N, 4.00.

Synthesis of *N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-phenylenediimine Chromium(III) Azide (4). Complex 3 (3.6 g, 6 mmol) was first dissolved in 250 mL of CH₃CN. Simultaneously, in another flask with a pressure-equalizing addition funnel, 1.1 equiv (1.3 g, 6.6 mmol) of AgClO₄ was dissolved in an equal volume of CH₃CN. The metal complex solution was transferred into the funnel and added dropwise over approximately 40 min. Immediate precipitation of AgCl was observed, and the reaction mixture was stirred overnight to ensure completion. The reaction mixture was then filtered into a flask already containing 3 equiv of NaN₃, to minimize exposure to air. Sodium azide has a low solubility in CH₃CN; thus, the reaction mixture was stirred for another 24 h. The mixture was diluted with diethyl ether, the organic phase was washed with copious amounts of water to remove NaClO₄ and the unreacted excess of NaN₃ and then dried with MgSO₄, and the solvent was removed in vacuo, yielding a brown powder (3.2 g, 84% yield). ATR ν (cm⁻¹): 2952 (s), 2905 (m), 2867 (m), 2099 (s), 2056 (m), 1601 (s), 1577 (s), 1521 (s), 1483 (m), 1461 (m), 1426 (s), 1256 (s), 1194 (s), 1171 (s), 1131 (m), 1023 (m), 867 (m), 837 (m), 786 (m), 746 (s), 536 (s). Anal. Calcd for C₃₆H₄₆N₅O₂Cr: C, 68.33; H, 7.33; N, 11.07. Found: C, 67.96; H, 7.99; N, 9.91.

Copolymerization of Cyclohexene Oxide and CO₂. Catalyst 1 (1 equiv, 63 mg) and the cocatalyst (1 equiv) were dissolved in 5 mL of CH₂Cl₂ and stirred at room temperature for at least 1.5 h, and then the solvent was removed under vacuum. A 35 mL portion (2500 equiv) of neat cyclohexene epoxide was added to the solid residue and the solution added via injection port into a 250 mL steel autoclave at ambient temperature that was previously dried in vacuo at 80 °C overnight. The autoclave was charged with the desired pressure of CO₂ 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 determination of conversion and selectivity by ¹H 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 dried in vacuo at 80 °C overnight.

Copolymerization of Propylene Oxide and CO₂. Catalyst 4 (1 equiv, 63.8 mg) and cocatalyst (0.5 equiv) were dissolved in 5 mL of CH₂Cl₂ and stirred at room temperature for at least 1.5 h, and then the solvent was removed under vacuum. A 35 mL portion (2500 equiv) of neat propylene epoxide was added to the solid residue and the solution added via injection port into a 250 mL steel autoclave at ambient temperature that was previously dried in vacuo at 80 °C overnight. The autoclave was charged with the desired pressure of CO₂ and heated to the reaction temperature. After the designated 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 determination of conversion and selectivity by ¹H NMR analysis, while the rest was extracted as a dichloromethane solution and precipitated in a MeOH/HCl (9/1) solution. The 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 Characterizations. All of the ¹H and ¹³C NMR spectra were acquired on a Bruker DMX 600 MHz NMR spectrometer in CD₂Cl₂ at 300 K.

Infrared spectra (FTIR-ATR) were recorded on a PerkinElmer Spectrum Two spectrometer. In a typical experiment, the catalyst and cocatalyst (cat:cocat = 1:1) were dissolved in 5 mL of dichloromethane for 1 h, and then the solvent was removed and the catalytic complex was analyzed by a PerkinElmer Spectrum Two spectrometer at room temperature. Later, cyclohexene oxide was added and, after 3.5 h, the solution was analyzed and the infrared spectra were recorded again under the same polymerization conditions.

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 flow. The sample concentration was set at 3 mg/mL and the injection volume at 150 μ L. Calibration of the curves used polystyrene standards in a 162–380000 g/mol range. Calorimetric curves were acquired on a PerkinElmer DSC 8000 instrument under nitrogen atmosphere, the samples being heated and chilled from –80 to 150 °C twice at 20 °C/min. Analytical elemental analyses was provided by Politecnico di Milano.

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Notes

The authors declare no competing financial interest.

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