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New Iron Pyridylamino-Bis(Phenolate) Catalyst for Converting CO_2 into Cyclic Carbonates and Cross-Linked Polycarbonates

Masoumeh Taherimehr,[a] João Paulo Cardoso Costa Sertã,[a] Arjan W. Kleij,[b, c] Christopher J. Whiteoak,[b] and Paolo P. Pescarmona*[a, d]

The atom-efficient reaction of CO_2 with a variety of epoxides has been efficiently achieved employing iron pyridylamino-bis(phenolate) complexes as bifunctional catalysts. The addition of a Lewis base co-catalyst allowed significant reduction in the amount of iron complex needed to achieve high epoxide conversions. The possibility of controlling the selectivity of the reaction towards either cyclic carbonate or polycarbonate was evaluated. An efficient switch in selectivity could be achieved when cyclic epoxides such as cyclohexene oxide and the seldom explored 1,2-epoxy-4-vinylcyclohexane were used as substrates. The obtained poly(vinylcyclohexene carbonate) presents pending vinyl groups, which allowed post-synthetic cross-linking by reaction with 1,3-propanedithiol. The cross-linked polycarbonate displayed a substantial increase in the glass transition temperature and chemical resistance, thus opening new opportunities for the application of these green polymers.

Introduction

Emissions of carbon dioxide (CO_2) as a consequence of human activity over the past two hundred years have resulted in an accumulation of approximately 1 teraton of this molecule in the atmosphere.[1] The high concentration of CO_2 may influence natural phenomena such as global temperature and the acidity of oceans and thus affect the environment.[2] This issue has prompted the international scientific community to pursue research attempting to mitigate the effects of the increased concentration of CO_2 in the atmosphere. Capture and sequestration of CO_2 have been proposed as a solution and this topic has seen significant investigation.[3] At the same time, the wide availability, renewability and non-toxicity of CO_2 has stimulated research aimed at employing this molecule as a renewable carbon resource to produce useful chemicals.[1,4–11] Since the carbon atom in CO_2 is in its highest oxidation state, conversion of CO_2 into chemicals requires a high energy input. The low free energy level of the molecule can be overcome by using a high free energy coupling partner such as hydrogen, unsaturated compounds, and small-ring heterocycles.[12–14] In this context, the atom-efficient reaction of CO_2 with epoxides to produce polymeric or cyclic carbonates is an attractive option for the utilization of CO_2 (Scheme 1).[15,16] Both possible products of the CO_2–epoxide coupling reaction have growing potential applications.[12,17] Cyclic carbonates can be employed as green solvents with attractive features as high polarity and low vapor pressure. They also find application as electrolytes in Li-ion batteries, and as intermediates for the synthesis of polymers and fine chemicals.[12] On the other hand, polycarbonates obtained from alternating co-polymerization of CO_2 and epoxides can be used in the synthesis of polyurethanes, thermoplastics and polymer resins.[5,17–19] These polycarbonates are considered green polymers not only for the use of CO_2 as feedstock in their production, but also for their biodegradability.[17] Several homogeneous and heterogeneous catalysts have been investigated to promote the CO_2–epoxide coupling reaction.[1,20–28] Typically, the catalytic system includes a nucleophile that is able to open the epoxide ring and a Lewis acid having the role of activating the epoxide towards the nucleophilic attack. After the formation of an alkoxide intermediate, CO_2 insertion into the metal-oxygen bond generates a carbonate intermediate that may undergo ring-closure to produce cyclic carbonate, or insert further CO_2 and epoxide molecules resulting in the growth of a CO_2–epoxide co-polymer chain.[29] During the co-polymerization, the consecutive insertion of two or more epoxides may also happen, which leads to the formation of ether linkages and thus affects the polymer properties (Scheme 1).

[a] M. Taherimehr, J. P. C. C. Sertã, Prof. P. P. Pescarmona
Centre for Surface Chemistry and Catalysis
University of Leuven, Kasteelpark Arenberg 23
3001 Heverlee (Belgium)

[b] Prof. A. W. Kleij, Dr. C. J. Whiteoak
Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16
43007 Tarragona (Spain)

[c] Prof. A. W. Kleij
Catalan Institute for Research and Advanced Studies (ICREA)
Pg. Lluís Companys 23
08010 Barcelona (Spain)

[d] Prof. P. P. Pescarmona
Chemical Engineering Department
University of Groningen
Nijenborgh 4
9747 AG Groningen (The Netherlands)
E-mail: p.p.pescarmona@rug.nl
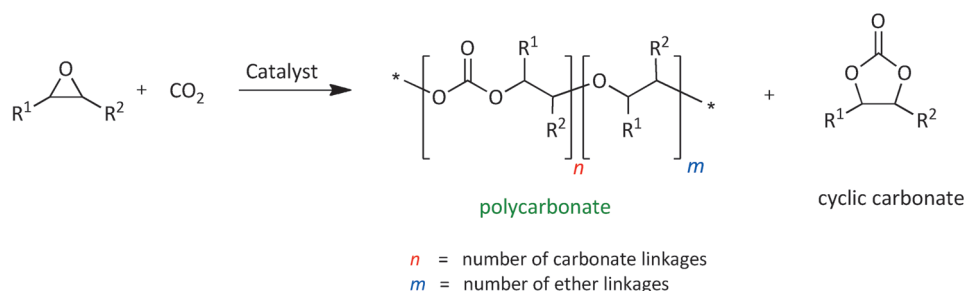
Scheme 1. The atom-efficient reaction of CO_2 with epoxides.

In this work, we present a study of iron(III) pyridylamino-bis(phenolate) complexes, FeX[O_2NN'], (X = Cl, Br) (Scheme 2) as novel homogeneous catalysts for the coupling reaction between CO_2 and a range of epoxides. Particular attention was

Scheme 2. The chemical structure of complex Fe^{III}X[O_2NN'].

dedicated to the investigation and control of the reaction selectivity towards either cyclic carbonates or polycarbonates, which entails careful tunin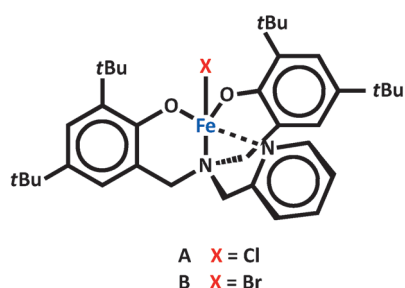g of the catalytic system and of the reaction conditions.[12,29] In the complex used in this study, the coordination of Fe^{III} to the pyridylamino-bis(phenol) ligand through two amino groups and two oxygen atoms implies a positive charge on the iron metal center, which is balanced by an anion that can act as a nucleophile. Therefore, it is anticipated that the use of these iron pyridylamino-bis(phenolate) complexes as catalysts can proceed without the need for adding a co-catalyst. This feature differentiates the Fe-complexes presented here from the neutral iron amino-triphenolate complexes, which have been reported to display excellent performance in the reaction of CO_2 with epoxides in combination with tetrabutylammonium halide co-catalysts.[29,30] In general, iron complexes have the advantage of being based on a non-toxic, widely available and inexpensive metal like iron.[31] Moreover, the iron pyridylamino-bis(phenolate) complexes can be obtained in virtually quantitative yields in a two-step procedure (See Scheme S1). Another important asset of these iron complexes is their air- and moisture-stability, which means that no inert conditions are required for their handling and storage. Additionally, no extra drying of the epoxide substrate is required and no specific equipment is needed to prevent the presence of adventitious water.

For the epoxide substrates that produced polycarbonates in the coupling reaction with CO_2, a detailed study of molar

mass, thermal properties, regio- and stereochemistry of the obtained polymer was carried out. In the case of poly(vinylcyclohexene carbonate), post-synthetic cross-linking of the polycarbonate with 1,3-propanedithiol was performed. This strategy was applied here for the first time to CO_2-based polycarbonates and proved very efficient in improving the thermal and mechanical properties of the polymer. This promising result opens new perspectives for the application of this class of green polycarbonates.

Results and Discussion

Two iron(III) pyridylamino-bis(phenolate) complexes with bipyramidal geometry in which Br or Cl occupy one apical site [FeX(O_2NN') with X = Cl or Br, see Scheme 2] were synthesized[32] and tested as novel homogeneous catalysts for the reaction of carbon dioxide with a broad scope of epoxides (see the Supporting Information and Figure S1–S4 therein for more details about the synthesis). Different organic salts were investigated as co-catalysts, that is, tetrabutylammonium salts (Bu$_4$NY, Y = Cl, Br, I, OAc) and bis(triphenylphosphoranylidene)ammonium chloride (PPNCl),[12] and the most relevant reaction conditions were studied by means of a tailored high-throughput reactor unit for performing reactions in supercritical CO_2 (see Figure S5).[33,34] This approach allowed the rapid and reliable investigation of the chosen set of parameters and, therefore, enabled a detailed screening of the catalytic properties of the iron complexes in the CO_2–epoxide coupling reactions. The target is to achieve high conversion of different epoxides with high selectivity to either the cyclic carbonate or the polycarbonate product. Both products are attractive, but synthesizing only one of them selectively would save undesirable work-up to separate them.

Cyclohexene oxide (CHO) was chosen as substrate for the first catalytic screening. This is a challenging substrate for the reaction with CO_2 because it has steric hindrance at both carbons of the epoxide ring on which the nucleophilic attack can occur. This epoxide also has a higher tendency to form polycarbonates compared to terminal epoxides (e.g., propylene oxide or 1,2-epoxyhexane) because the geometric strain of the two connected rings of cis-cyclohexene carbonate limits the formation of this product. All the catalytic tests were conducted in supercritical carbon dioxide (scCO$_2$) medium without any additional solvent. It is worth pointing out that employing scCO$_2$ can improve the interaction between reagents and catalysts and generally results in higher epoxide conversion and high carbonate linkages percentage in the poly(cyclohexene carbonate) chains.[29] The iron catalyst **A** (X = Cl) or **B** (X = Br) are both able to act as bifunctional catalyst to promote the reaction between cyclohexene oxide and CO_2 (Table 1, entries 1 and 18). The halide in apical position acts as the nucleophile to

Table 1. Catalytic screening of complexes **A** and **B** in the reaction of cyclohexene oxide (CHO) with CO_2.[a]

Entry	Catalyst/co-catalyst type	loading[b] [mol %]	Metal/nucleophile	Epoxide conversion[c] [%]	Selectivity[d] [%] polycarbonate	cyclic carbonate	Carbonate linkages[e] [%]	TON[f]	M_n[g] [g mol^{-1}]	PDI[h] (M_w/M_n)
1	**A**/–	5:0	1:1	79	88	12	–	16	–	–
2	''	0.5:0	1:1	11	85	15	–	22	–	–
3	**A**/Bu$_4$NCl	0.5:0.5	1:2	60	82	18	96	120	1418	1.1
4	''	0.5:1	1:3	59	64	36	94	118	1012	1.2
5	''	0.5:5	1:11	56	17	83	–	112	–	–
6	**A**/Bu$_4$NBr	0.5:0.5	1:2	63	60	40	–	126	–	–
7	''	0.5:1	1:3	76	32	68	–	190	–	–
8	''	0.5:5	1:11	95	0	>99	–	200	–	–
9	**A**/Bu$_4$NI	0.5:0.5	1:2	12	60	40	–	24	–	–
10	''	0.5:1	1:3	44	56	44	–	88	–	–
11	''	0.5:5	1:11	63	9	91	–	126	–	–
12	**A**/Bu$_4$NOAc	0.5:0.5	1:2	10	86	14	–	20	–	–
13	''	0.5:1	1:3	11	69	31	–	22	–	–
14	''	0.5:5	1:11	42	15	85	–	84	–	–
15	**A**/PPNCl	0.5:0.5	1:2	49	81	19	>99	98	704	1.1
16	''	0.5:1	1:3	52	49	51	>99	104	903	1.2
17	''	0.5:5	1:11	59	5	95	–	118	–	–
18	**B**/–	5:0	1:1	67	79	21	–	13	–	–
19	**B**/Bu$_4$NCl	0.5:0.5	1:2	13	41	59	–	26	–	–
20	**B**/Bu$_4$NBr	0.5:0.5	1:2	19	32	68	–	20	–	–
21	–/Bu$_4$NCl	0:0.5	–	3	0	>99	–	–	–	–
22	–/Bu$_4$NBr	0:0.5	–	4	0	>99	–	–	–	–

[a] Reaction conditions: 60 °C, 80 bar, 18 h, 15 mmol CHO, 3 mmol mesitylene as internal standard for NMR analysis. [b] Relative to the epoxide. [c] Based on ^{1}H NMR analysis of the reaction mixture (see Figure S6 for an example). [d] Based on ^{1}H NMR and FTIR analysis. [e] Based on ^{1}H NMR analysis of the purified co-polymer (see Figure S7 for an example). [f] Turnover number, defined as mol$_{converted\ epoxide}$/mol$_{Fe}$. [g] Determined by GPC in THF at 30 °C against polystyrene standards. [h] Polydispersity index defined as PDI = M_w/M_n.

attack the coordinated epoxide, as it is shown in the postulated mechanism (Scheme S2). In both cases, the polycarbonate is the major product, though cyclic carbonate was also observed. Higher activity and higher selectivity towards polycarbonates was obtained using catalyst **A**. The difference in activity can be explained by the larger radius of bromide compared to chloride, which may impose a higher degree of steric repulsion for the incoming epoxide substrate when approaching the iron center, thus reducing the reaction rate. On the other hand, the observed higher selectivity towards polycarbonates with catalyst **A** is the result of the poorer leaving ability of Cl$^-$ compared to Br$^-$. This means that the growth of the polycarbonate chain with chloride terminal groups is favored over ring closure ("back-biting"), which would lead to cyclic carbonate formation and liberate a halide anion (Scheme S2).[12]

To improve the efficiency of the catalytic system, the ratio between the iron complex and nucleophile was increased by adding different (external) organic halides as co-catalysts (binary catalytic system). The addition of a co-catalyst allows significant reduction in the concentration of iron complex needed to achieve high epoxide conversion (Table 1, compare entries 1, 2 and 3). Tuning the nucleophilicity of the anion of the organic salt and varying the ratio between the iron complex and the organic salt are tools to optimize the activity and control the product selectivity in the CO_2–epoxide coupling reaction.[12] Experiments performed with NBu$_4$Br and NBu$_4$Cl as co-catalysts evidence the higher activity of complex **A** compared to complex **B** (Table 1, entries 3 and 19, entries 6 and

20), as already observed in the tests with the complex alone. With ammonium salts and catalyst **A** in 1:1 ratio (0.5 mol %) the dependency of the activity on the type of anion shows the trend OAc~I<Cl~Br (Table 1). These results suggest that the catalytic activity increases by decreasing the size of the nucleophilic anion, as a result of less steric hindrance in the nucleophilic attack in the first step of the reaction. The high selectivity towards the polycarbonate when chloride and acetate salts are employed as co-catalysts (Table 1, entries 3 and 12) originates from the poor leaving ability of these species.[12] However, full selectivity towards the polycarbonate could not be achieved (Table 1).

The selectivity towards the cyclic carbonate can be enhanced not only by improving the leaving ability of the nucleophile (vide supra) but also by increasing the nucleophile-to-metal ratio, which facilitates the displacement of the metal-bound carbonate intermediate by a new nucleophilic anion, thus favoring the ring-closure reaction.[12, 16] The effect of the relative amount of the co-catalyst was studied by employing three different ratios between the catalyst **A** and each of the co-catalysts (1:1, 1:2, and 1:10). As anticipated, an increase in the nucleophile to metal ratio leads to higher selectivity towards cyclic carbonate (see the following groups of entries in Table 1: 3–5; 6–8; 9–11; 12–14; 15–17). With NBu$_4$Br, an excellent 95 % epoxide conversion with complete selectivity towards cyclic carbonate production was achieved (Table 1, entry 8).

The effect of the cation of the co-catalyst was examined by comparing PPNCl with Bu$_4$NCl. (Table 1 entries 3–5 and en-

tries 15–17). Similar activity and selectivity trends are observed with these two co-catalysts, but slightly higher selectivity for cyclic carbonate was obtained with PPNCl. This behavior is opposite to what generally observed with these two chloride salts.[29] It can be hypothesized that the PPN$^+$ cation remains in the vicinity of the chloride anion that attacked the epoxide due to the interaction of the phenyl rings in PPN$^+$ with the phenyl rings of the iron complex. This proximity facilitates the displacement of chloride from the carbonate intermediate, thus leading to a higher selectivity towards cyclic carbonate.

The poly(cyclohexene carbonate)s obtained in this work are characterized by low molar mass (see M_n in Table 1) and for the reactions with higher concentration of co-catalyst only small oligomers are generated that cannot be separated by precipitation with acidified methanol. The low molar mass of these poly(cyclohexene carbonate)s can be ascribed to the competition between polymer growth and cyclic carbonate formation and to the presence of adventitious water in the system, which can cause chain termination.[17,29] The low molar mass of these short-chain polycarbonates coupled with their narrow molar mass distribution (cf. low PDI values in Table 1) makes them suitable for application as diols in the synthesis of polyurethanes.[5,17,19]

To fully appreciate the catalytic activity of the iron pyridyl-amino-bis(phenolate) complexes, it is important to note that when Bu$_4$NBr or Bu$_4$NCl were employed alone under the same conditions (60 °C, 80 bar, 18 h), the conversion of CHO was less than 5 % compared to values higher than 60 % in the presence of the Fe-complex (Table 1, compare entries 21 and 22 to entries 3 and 6).

The effect of increasing the reaction temperature from 60 to 85 °C was evaluated with different catalyst to co-catalyst ratios in the reaction of CO_2 with CHO employing complex **A** and NBu$_4$Br (Table 2, entries 1–3). The reaction time was decreased to 3 h to allow comparison at moderate conversions. Since five-membered cyclic carbonates are the thermodynamic products of the CO_2–epoxide coupling reaction, increasing the temperature leads to an increase in the selectivity towards cyclic carbonates (compare Table 2, entries 1 and 2 with Table 1, entries 6 and 7). The reaction with a cat./co-cat. ratio of 1:10 gives full conversion with complete selectivity towards cyclic

carbonate (Table 2, entry 3). Similar trends were observed with PPNCl as co-catalyst. Decreasing the molar loading of catalyst and PPNCl to half the amount of entry 1 leads to slightly higher TON, whereas the selectivity is nearly unaltered (Table 2, entries 6 and 7). When comparing the catalytic performance of complex **A** with that of the previously reported iron amino-tri-phenolate complexes under the same reaction conditions and the same loading of catalyst and co-catalyst,[29] it is observed that the iron pyridylamino-bis(phenolate) complex reported here displays higher activity and selectivity when the target product is cyclohexene carbonate (Table 2, entry 3), whereas both activity and selectivity are lower under reaction conditions aimed at obtaining the polycarbonate (Table 2, entry 7). The lower selectivity of complex **A** towards the formation of poly(cyclohexene carbonate) is attributed to the lower metal/nucleophile ratio (1:2) compared to that with the iron amino-triphenolate complexes (1:1) when the complex and the co-catalyst are employed in 1:1 ratio. The higher relative amount of nucleophile favors the displacement of the metal-bound carbonate intermediate,[16] thus leading to the observed higher selectivity towards the cyclic carbonate product.

Water that might be present as impurity can interact with the metal center and thus affect the activity of the catalyst: it has been reported that the presence of water can substantially decrease the activity of binary catalytic systems as well as the selectivity towards polycarbonate and its molar mass.[35] To study the effect of H_2O on our catalytic system, different amounts of water were added in the reaction catalyzed by **A**/Bu$_4$NBr. The decrease in activity from 63 %, (Table 2, entry 2), to 7 % with 10 % of water (Table 2, entry 4), and to 0 % when 50 % of water was added (entry 5) demonstrates that water has a detrimental effect on the catalytic activity of complex **A**.

The next step in our study was to evaluate the versatility of the catalyst with another challenging substrate, namely 1,2-epoxy-4-vinylcyclohexane (VCHO). Similarly to CHO, this substrate is anticipated to display high selectivity towards polycarbonate formation. VCHO is largely unexplored as substrate for co-polymerization with CO_2. We selected it for this work because the vinyl functionality offers the attractive opportunity of post-polymerization modifications.[12,36] VCHO was tested with catalyst **A** and various co-catalysts at 60 °C, 80 bar, 18 h

Table 2. Catalytic screening of complex **A** in the reaction of cyclohexene oxide (CHO) with CO_2.[a]

Entry	Catalyst/co-catalyst type	loading[b] [mol %]	Metal/nucleophile	Epoxide conversion[c] [%]	Selectivity[d] [%] polycarbonate	cyclic carbonate	Carbonate linkages[e] [%]	TON[f]	M_n[g] [g mol^{-1}]	PDI[h] (M_w/M_n)
1	**A**/Bu$_4$NBr	0.5:0.5	1:2	50	40	60	–	100	1351	1.0
2	''	0.5:1	1:3	63	26	74	>99	126	1145	1.0
3	''	0.5:5	1:11	>99	0	>99	–	200	–	–
4[i]	''	0.5:1	1:3	7	0	>99	–	14	–	–
5[j]	''	0.5:1	1:3	0	–	–	–	–	–	–
6	**A**/PPNCl	0.25:0.25	1:2	32	63	37	>99	128	808	1.1
7	''	0.5:0.5	1:2	54	60	40	>99	108	1612	1.1

[a] Reaction conditions: 85 °C, 80 bar, 3 h, 15 mmol CHO, 3 mmol mesitylene. [b] Relative to the epoxide. [c] Based on ^{1}H NMR analysis of the reaction mixture. [d] Based on ^{1}H NMR and FTIR analysis. [e] Based on ^{1}H NMR spectra of the purified co-polymer. [f] Turnover number, defined as mol$_{converted\ epoxide}$/mol$_{Fe}$. [g] Determined by GPC in THF at 30 °C against polystyrene standards. [h] Polydispersity index defined as PDI = M_w/M_n. [i] 10 mol % H_2O (relative to the epoxide) were added to the reaction mixture. [j] 50 mol % H_2O (relative to the epoxide) were added to the reaction mixture.

Table 3. Catalytic screening of complexes **A** and **B** in the reaction of 1,2-epoxy-4-vinylcyclohexane (VCHO) with CO_2.[a]

Entry	type	Catalyst/co-catalyst loading[b] [mol%]	Metal/nucleophile	Epoxide conversion[c] [%]	Selectivity[d] [%] polycarbonate	cyclic carbonate	Carbonate linkages[e] [%]	TON[f]	M_n[g] [g mol^{-1}]	PDI[h] (M_w/M_n)
1	**A**/Bu$_4$NCl	0.5:0.5	1:2	48	98	2	86	96	1995	1.2
2	''	0.5:1	1:3	30	67	33	–	60	–	–
3	''	0.5:5	1:11	53	49	51	–	106	–	–
4	**A**/Bu$_4$NBr	0.5:0.5	1:2	27	78	22	–	54	–	–
5	''	0.5:1	1:3	50	48	52	–	100	–	–
6	''	0.5:5	1:11	92	0	>99	–	184	–	–
7	**A**/Bu$_4$NOAc	0.5:0.5	1:2	18	99	1	–	36	–	–
8	''	0.5:1	1:3	37	96	4	–	74	–	–
9	''	0.5:5	1:11	35	48	52	–	70	–	–
10	**A**/PPNCl	0.5:0.5	1:2	39	95	5	>99	78	932	1.2
11	''	0.5:1	1:3	43	70	30	–	86	–	–
12	''	0.5:5	1:11	48	45	55	–	96	–	–
13	**B**/Bu$_4$NCl	0.5:0.5	1:2	14	69	41	–	28	–	–

[a] Reaction conditions: 60 °C, 80 bar, 18 h. 15 mmol VCHO, 3 mmol mesitylene. [b] Relative to the epoxide. [c] Based on ^{1}H NMR analysis of the reaction mixture (see Figure S8 for an example). [d] Based on ^{1}H NMR and FTIR analysis. [e] Based on ^{1}H NMR of the purified co-polymer (see Figure S9 for an example). [f] Turnover number, defined as mol$_{converted\ epoxide}$/mol$_{Fe}$. [g] Determined by GPC in THF at 30 °C against polystyrene standards. [h] Polydispersity index defined as PDI = M_w/M_n.

(Table 3). The catalytic activity and product selectivity in the CO_2–VCHO reaction follow similar trends as those observed for the CO_2–CHO coupling reactions, as exemplified by the increase in selectivity towards the cyclic carbonate with higher relative amount of co-catalyst. However, higher selectivity towards the polycarbonate was obtained compared to the reaction of CHO with CO_2 under each set of conditions. Virtually complete selectivity towards poly(vinylcyclohexene carbonate) was achieved with OAc$^-$ and Cl$^-$ as nucleophiles and a Fe-complex/nucleophile ratio of 1:1, with the latter nucleophile giving significantly higher conversion (Table 3, entries 1 and 7).[17] The higher nucleophilicity and smaller size of the chloride compared to the acetate anion explain the observed difference in activity. The quality of the obtained polycarbonate in terms of content of carbonate linkages was higher when PPNCl was employed as co-catalyst compared to Bu$_4$NCl (Table 3, entries 1 and 10). With PPNCl as co-catalyst the obtained polycarbonate exclusively contained carbonate linkages (no ether linkages) whereas the polymer obtained in the presence of Bu$_4$NCl as co-catalyst contained 14% ether linkages, as detected by ^{1}H NMR and FTIR spectroscopy (Figure S10, S11). Remarkably, the selectivity of the reaction between VCHO and CO_2 could be completely switched by using Bu$_4$NBr as co-catalyst and

performing the reaction with a catalyst-to-co-catalyst ratio of 1:10. Under these conditions, full selectivity towards the cyclic carbonate was achieved, with an excellent epoxide conversion of 92% (Table 3, entry 6). These results show that in the reaction of VCHO with CO_2 catalyzed by complex **A**, tuning the type and relative amount of co-catalyst allows efficiently switching the reaction selectivity between exclusive polymeric or exclusive cyclic carbonate formation. Similarly to what observed with CHO as substrate, higher selectivity towards cyclic carbonate was attained in the CO_2–VCHO coupling reaction by increasing the reaction temperature from 60 °C to 85 °C (compare Table 3 and Table 4). Increasing the conversion of VCHO in the reaction catalyzed by complex **A**/PPNCl by performing the reaction at 85 °C for 18 h also leads to a substantial increase in the polycarbonate molar mass: from $M_n =$ 2086 g mol^{-1} (PDI = 1.2) after 3 h to $M_n = 3784$ g mol^{-1} (PDI = 1.4) (see Table 4, entries 5 and 6). In line with what found with CHO, the polycarbonate selectivity is largely unaffected by increasing the catalyst and co-catalyst loading while keeping their ratio constant (Table 4, entries 3–5).

The potential of complex **A** as homogeneous catalyst for the reaction of CO_2 with epoxides was further evaluated employing a wide scope of substrates. Styrene oxide (SO) is generally

Table 4. Catalytic screening of complex **A** in the reaction of 1,2-epoxy-4-vinylcyclohexane (VCHO) with CO_2.[a]

Entry	Time [h]	type	Catalyst/co-catalyst loading[b] [mol%]	Metal/nucleophile	Epoxide conversion[c] [%]	Selectivity[d] [%] polycarbonate	cyclic carbonate	Carbonate linkages[e] [%]	TON[f]	M_n[g] [g mol^{-1}]	PDI[h] (M_w/M_n)
1	3	**A**/Bu$_4$NBr	0.5:0.5	1:2	29	49	51	66	58	–	–
2	3	''	0.5:1	1:3	24	35	65	–	48	–	–
3	3	**A**/PPNCl	0.25:0.25	1:2	18	78	22	77	72	–	–
4	3	''	0.5:0.5	1:2	34	79	21	85	68	1840	2.0
5	3	''	1:1	1:2	69	73	27	>99	69	2086	1.2
6	18	''	1:1	1:2	84	77	23	>99	84	3784	1.4

[a] Reaction conditions: 85 °C, 80 bar, 3 h or 18 h.15 mmol VCHO, 3 mmol mesitylene. [b] Relative to the epoxide. [c] Based on ^{1}H NMR analysis of the reaction mixture. [d] Based on ^{1}H NMR and FTIR analysis. [e] Based on ^{1}H NMR spectra of the purified co-polymer. [f] Turnover number, defined as mol$_{converted\ epoxide}$/mol$_{Fe}$. [g] Determined by GPC in THF at 30 °C against polystyrene standards. [h] Polydispersity index defined as PDI = M_w/M_n.

reported as a relatively sluggish substrate in the reaction with carbon dioxide compared to other terminal epoxides.[17] Complex **A** was used as catalyst in combination with a tetrabutylammonium halide, because these readily available co-catalysts gave the best performance with CHO and VCHO as substrates (vide supra). Full selectivity towards styrene carbonate was obtained in all the tests. For this reaction, the activity order as a function of the co-catalyst is $Bu_4NI > Bu_4NBr > Bu_4NCl$ (Table 5), which corresponds to the trend of leaving ability of the halides. An excellent conversion (92%) was achieved with complex **A**/Bu_4NI at 60°C (Table 5, entry 3). For the reaction of CO_2 with a range of other epoxides including two natural products (the terpene-based substrates in Table 6 entries 8 and 9) and oxetane, complex **A** was employed in combination with Bu_4NBr (Table 6). This co-catalyst is often reported as a suitable co-catalyst for the synthesis of cyclic carbonates due to the balance between nucleophilicity and leaving ability of the bromide anion.[12]

Good to excellent conversions were achieved with the terminal epoxides at 85°C, 80 bar and using a reaction time of 3 h, demonstrating the versatility of catalyst **A** (Table 6, entries 1–4). The lower ring strain of oxetane represents a drawback in its reaction with CO_2 because it makes the ring opening step more difficult, and this is illustrated by the low activity in the conversion of this substrate (Table 6, entry 7). The presence of a methanetetrayl group on the epoxide ring imposes a significant steric barrier to the nucleophilic attack, and this explains the lack of success when attempting to react limonene oxide (Table 6, entry 8) and α-pinene oxide (Table 6, entry 9).

Microstructure and properties of polycarbonates

For the substrates that could be converted into polycarbonate that could be isolated (i.e., in the case of CHO and VCHO) the physicochemical properties of the polymers were investigated. $^{13}C\{^1H\}$ NMR analysis of purified polycarbonate allowed to determine the regio- and stereo-selectivity of the co-polymerization reaction. With CHO as substrate, the $^{13}C\{^1H\}$ NMR spectrum of the carbonate region shows signals corresponding to syndiotactic junctions (at $\delta = 153.2$ ppm), isotactic junctions (at $\delta = 153.8$ ppm) and a signal at $\delta = 154.3$ ppm, which is assigned to carbonate junctions located in proximity of hydroxyl-terminated ends of the chain (see Figure S12 in the Supporting Information).[37,38] The assignment of this peak is in agreement with the low M_n observed for the polycarbonates reported in

Table 6. Substrate screening with catalyst **A** in the reaction with CO_2.[a]

Entry	Substrate	Epoxide conversion[b] [%]	Selectivity[c] [%] polycarbonate	Selectivity[c] [%] cyclic carbonate	TON[d]
1		>99	0	>99	200
2		96	0	>99	192
3		88	0	>99	176
4		56	0	>99	112
5		50	40	60	100
6		29	49	51	58
7		7	0	>99	14
8		0	–	–	0
9		0	–	–	0

[a] Reaction conditions: 85°C, 80 bar, 3 h, catalyst 0.5 mol%, co-catalyst Bu_4NBr 0.5 mol%, epoxide 15 mmol, mesitylene 3 mmol (mol% relative to the epoxide). [b] Based on ^1H NMR analysis of the reaction mixture. [c] Based on ^1H NMR and FTIR analysis. [d] Turnover number, defined as $mol_{converted\ epoxide}/mol_{Fe}$.

this work. The low intensity peak at $\delta = 155.1$ ppm might indicate the presence of a small amount of terminal carbonate groups.[37] These results indicate that atactic poly(cyclohexene carbonate) was formed, as expected considering the non-chiral nature of the catalyst, and show that the polymer is mainly terminated with hydroxyl groups.[17]

In the reaction of CO_2 with VCHO, the formation of atactic polymer chains is evidenced by the complex signal in the region between $\delta = 153.2$ and 153.5 ppm of the $^{13}C\{^1H\}$ NMR spectrum (Figure S13). Head-to-tail (HT) regio-regular sequences (Scheme 3) are expected to be favored over tail-to-tail (TT) and head-to-head (HH) regio-regular sequences because they would lead to lower steric hindrance between the pending vinyl groups of adjacent repeating units. Since VCHO has four different stereoisomers (Scheme 3), a polymer with exclusively HT regio-regular sequences would have ten possible stereo-sequences and thus generate a complex signal in the carbonate region of the ^{13}C NMR spectrum, as the one observed in this work. However, based on the current data it cannot be excluded that TT and HH regio-regular sequences are also present. In analogy with the polycarbonate based on CHO, the low intensity peak at $\delta = 153.9$ ppm is assigned to carbonate junctions located in proximity of hydroxyl-terminated ends of the chain (Figure S13).

Table 5. Catalytic screening of complex **A** in the reaction of styrene oxide (SO) with CO_2.[a]

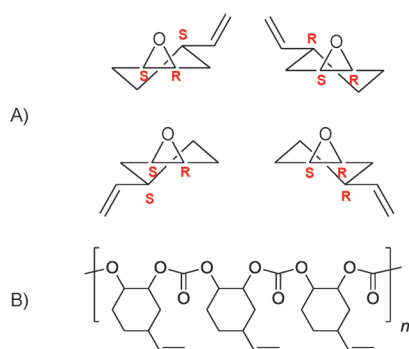| Entry	Catalyst/co-catalyst	Epoxide conversion[b] [%]	TON[c]
1	**A**/Bu_4NCl	28	56
2	**A**/Bu_4NBr	73	146
3	**A**/Bu_4NI	92	184

[a] Reaction conditions: 60°C, 80 bar, 18 h, 15 mmol SO, 3 mmol mesitylene, catalyst 0.5 mol%, co-catalyst 0.5 mol% (mol% relative to the epoxide). [b] Based on ^1H NMR analysis of the reaction mixture. [c] Turnover number, defined as $mol_{converted\ epoxide}/mol_{Fe}$.

Scheme 3. A) Stereoisomers of 1,2-epoxy-4-vinyl-cyclohexane, B) Head-to-tail PVCHC chain structures.

Scheme 4. Schematic representation of the free-radical cross-linking of PVCHC.

Improvement of the physical properties of PVCHC by cross-linking

The presence of functional groups on the polycarbonate back-bone offers the possibility of post-polymerization modifications that enable tailoring the physicochemical features of the polymer such as hydrophilicity, solubility, biodegradability and thermal and mechanical properties.[17,39] Cross-linking generates networks by interconnecting the polymer chains and, therefore, can be employed to increase the molar mass, the chemical resistance, and the stability against elevated temperatures and mechanical deformation of the polymers. This strategy is applied here for the first time to poly(vinylcyclohexene carbonate) [PVCHC] by connecting the polymer chains through the pendant double bond of the vinyl groups. For this purpose, the purified polycarbonate (obtained form the reaction mentioned in entry 1, Table 3) was reacted with 1,3-propanedithiol in the presence of the radical initiator azobisisobutyronitrile (AIBN) (thiol-ene reaction, see Scheme 4). The successful cross-linking was demonstrated by the disappearance of the peaks of the double bond of the vinyl group in the solid-state $^{13}C\{^1H\}$ NMR spectrum of the cross-linked material (Figure S14 in the Supporting Information). As a result of the cross-linking, the glass transition temperature (T_g) of the polymer shows a considerable improvement of 55 °C from 75 to 130 °C, as measured by DSC analysis (Figure S15 in Supporting Information). The cross-linked polymer also displays enhanced chemical resistance, as indicated by its insolubility in (hot) THF, DMF, acetone, ethanol, CHO or propylene carbonate. SEM images show that the morphology of the cross-linked PVCHC differs significantly from that of PVCHC (Figure 1 and 2). The new morphology might arise from nucleation during dissolution of PVCHC in ethanol followed by particle growth through cross-linking.[40] The observed properties of the thermosetting polymer obtained by cross-linking PVCHC are promising for a potential application as engineering plastic.[41] Further investigation will aim at tuning the physicochemical properties of these polymers by varying the degree of cross-linking by changing the 1,3-propanedithiol loading. This work will also involve a study of the increase in stiffness and thermal resistance as a function of the cross-linking degree.
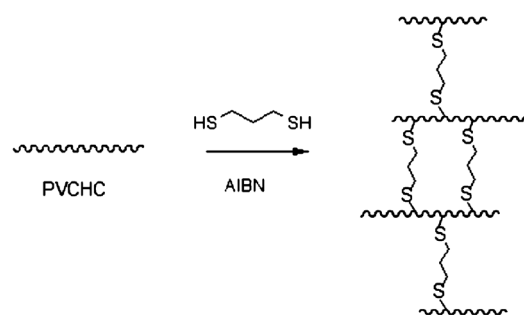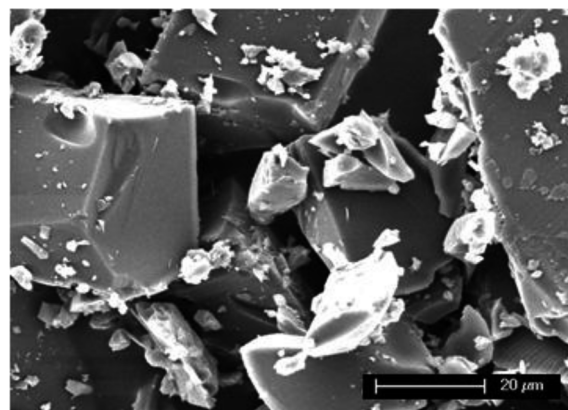

Figure 1. SEM image of PVCHC after re-precipitation and drying in a Schlenk line.
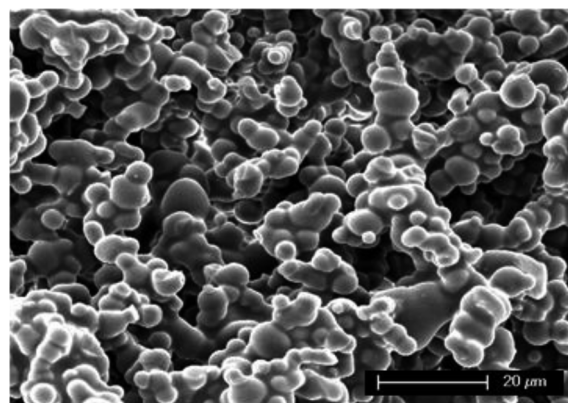
Figure 2. SEM image of dried cross-linked PVCHC.

Conclusions

Fe[III]X[pyridylamino-bis(phenolate)] complexes (X = Cl, Br), alone or in combination with ionic Lewis bases, have been evaluated as homogeneous catalysts for the coupling reaction of CO_2 and epoxides. The catalytic system has been shown to be versatile in the conversion of a broad scope of epoxides. Besides displaying high activity, the FeCl[O₂NN'] catalyst is remarkably robust, and unpurified substrates can be used without concerns for the presence of water impurities in the reaction set-up. The parameters governing the selectivity of the reaction

towards cyclic or polymeric carbonate were studied and optimized to control and maximize the selectivity towards each of the two valuable products. With terminal epoxides, the cyclic carbonate was the main product, whereas with CHO and the less explored VCHO as substrates it was also possible to selectively obtain polycarbonates with high percentage of carbonate linkages. Particularly, for the reaction of VCHO with CO_2 it was possible to fully switch the selectivity of the reaction between cyclic to polymeric carbonate by tuning the type and relative amount of organic salt employed as Lewis base. The obtained PVCHC was efficiently cross-linked with 1,3-propanedithiol. This new strategy proved effective in increasing the glass transition temperature of the polymer by 55 °C and rendering it insoluble in organic compounds. Cross-linked PVCHC is a thermosetting polymer that may find applications as engineering plastic.

Experimental Section

Materials

2,4-di-*tert*-butylphenol (99% purity), 2-picolylamine (99% purity), aqueous formaldehyde (37 wt% in H_2O), anhydrous iron(III)chloride ($FeCl_3$ 99.99% purity), anhydrous iron(III) bromide ($FeBr_3$ 99.99% purity), tetrabutylammonium iodide (Bu_4NI, 98% purity), tetrabutylammonium bromide (Bu_4NBr, 98% purity), tetrabutylammonium chloride (Bu_4NCl, 98% purity), Bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) (98% purity), mesitylene (98% purity), cyclohexene oxide (CHO, 98% purity), styrene oxide (SO, 97% purity), 1,2-epoxy-4-vinylcyclohexane (VCHO, 98% purity), glycidyl methacrylate (97% purity), *tert*-butyl glycidyl ether (99% purity), glycidyl isopropyl ether (98% purity), 1,3-trimethylene oxide (97% purity), α-pinene oxide (97% purity), (+)-limonene oxide (97% purity), azobisisobutyronitrile (AIBN) (99% purity), and 1,3-propanedithiol (99% purity), unstabilized THF (99.8% purity) and solvents [diethyl ether, tetrahydrofuran (THF), methanol (MeOH), toluene] were purchased from Sigma–Aldrich and used without further purification. Deuterated chloroform ($CDCl_3$) (>99.6 atom%), as solvent for ^1H NMR and $^{13}C\{^1H\}$ NMR measurements, was purchased from Acros Organics.

Synthesis of the pyridylamino-bis(phenol), $H_2[O_2NN']$ ligand

The ligand was synthesized following a previously reported procedure involving the reaction of 2,4-di-*tert*-butylphenol, 2-picolylamine and formaldehyde.[32] The identity of the compound was determined by ^1H NMR and FTIR spectroscopy.[32] The details of the synthesis and characterization are provided in the Supporting Information.

Synthesis of the iron(III) pyridylamino-bis(phenolate), $FeCl[O_2NN']$ and $FeBr[O_2NN']$ complexes

The synthesis of the iron(III) pyridylamino-bis(phenolate) complexes was performed following a previously reported procedure, which involves the reaction of the ligand $H_2[O_2NN']$ with the selected iron salt (anhydrous $FeCl_3$ or anhydrous $FeBr_3$) in 1:1 ratio in methanol solution and in the presence of triethylamine as a HX scavenger (X = Cl, Br).[32] The formation of the desired $FeCl[O_2NN']$ and $FeBr[O_2NN']$ complexes was monitored by means of FTIR and

UV/Vis.[32] Full details of the synthesis and characterization of the complexes can be found in the Supporting Information.

Catalytic tests, synthesis of cyclic and/or polymeric carbonates

The catalytic tests were performed in a high-throughput unit (Integrated Lab Solution, ILS) consisting of 24 batch reactors (see Figure S5) that can operate simultaneously at temperature up to 180 °C and CO_2 pressure up to 180 bar. A detailed description of this unit can be found elsewhere.[33,34] For each experiment, the catalyst, co-catalyst, the selected epoxide (15 mmol) and mesitylene (3 mmol) as the NMR internal standard were weighed and added to a glass vial along with a magnetic stirring bar. The vials were sealed with a plastic cap containing a silicon rubber seal where two needles were inserted for the CO_2 gas to enter and circulate through the vial. After closing the reactor, all the steps to reach the required reaction conditions were controlled using tailored software (ProControl). First, the reactors were purged with N_2 and CO_2 to remove air. Then, the exit valves were closed and the reactors were pressurized with CO_2 (99.995% purity, supplied by Air Liquide). For the reactions at a pressure of 80 bar and a temperature of 85 °C, carbon dioxide was pumped until the pressure inside the reactor reached ~70 bar while the temperature was increased to 85 °C. Next, the reactor was further pressurized until the target value of 80 bar was reached inside the reactors, at which point the valve connecting the reactor and the main line was closed. Similar protocols were followed for the reactions at 60 °C. The start of each reaction was defined as the moment at which the selected reaction conditions were reached and the magnetic stirring was turned on at 900 rpm. After the required reaction time, the stirring was turned off and the reactor was cooled down until it reached 30 °C (which takes about 2 h). Then, the depressurization process was initiated and continued until the pressure inside the reactor was below 2 bar (these conditions were reached in about further 2 h). Finally, the reactor block was opened and the glass vials were removed from the block. 50 μL of each reaction mixture were diluted with 600 μL of $CDCl_3$ to measure the ^1H NMR spectra to calculate the conversion (examples of these ^1H NMR spectra are presented in the Supporting Information). To determine the product selectivity, one drop of the reaction mixture was diluted with ethanol and placed on a KBr plate, which was used for analysis by infrared spectroscopy (FTIR). The selectivity towards cyclic or polymeric carbonate was determined on the basis of the C=O absorption band, which is observed at ~1800 cm^{-1} for the cyclic carbonate and at ~1750 cm^{-1} for the polycarbonate.[17,29] Acidified methanol (1 M of HCl in methanol) was added to the samples containing polycarbonate, as determined by FTIR, to precipitate the polymer. The liquid was separated using a pipette and the remaining viscous polycarbonate was placed in a Schlenk-line to vacuum-dry overnight. Around 10 mg of the obtained powder was dissolved in 600 μL $CDCl_3$ and analyzed by ^1H NMR spectroscopy to determine the number of repeating units, and by $^{13}C\{^1H\}$ NMR spectroscopy to determine the stereoselectivity. 20 mg of polycarbonate were dissolved in 500 μL of unstabilized THF to measure the mass average molar mass (M_w) and the number average molar mass (M_n) by gel-permeation chromatography (GPC).

Poly(4-vinyl-1,2 cyclohexene carbonate) cross-linking reaction

PVCHC obtained form the reaction mentioned in Table 3, entry 1 (1000 mg corresponding to ~6 mmol of the 1,2-epoxy-4-vinylcyclo-

hexane), 1,3-propanedithiol (3 mmol), azobisisobutyronitrile (90 mg) as radical initiator, and ethanol were weighed in a three-neck round-bottom flask. Argon was bubbled for 10 min and the mixture was stirred for 20 h under Ar at 78 °C. After cooling to room temperature, the foam-like solid (see Figure S16 in Supporting Information) was filtered, washed with hot methanol and then dried in a vacuum oven at 40 °C overnight.[34]

Characterization

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were measured on a Bruker Advance 300 MHz spectrometer. FTIR spectra were obtained using a Bruker IFS66v/S spectrometer equipped with a vacuum chamber chargeable with liquid nitrogen. Gel permeation chromatography (GPC) measurements were performed utilizing a Shimadzu 10 A apparatus with a mixed D-column: 5 μm (medium to high M_n) maintained at 30 °C, and with two tunable absorbance detectors (set at a wavelength of 250 nm and 300 nm) or a refractive index detector (RID). The instrument was calibrated with polystyrene standards. The morphology of polymers was studied by scanning electron microscopy (SEM) on a Philips XL 30 FEG with an acceleration voltage of 10 kV and working temperature of the emitter of 1800 K. Differential scanning calorimetry (DSC) analysis was performed on a Q2000 DSC (TA Instruments) by cycling between 20 and 200 °C with heating/cooling rates of 20 °C min^{-1} under N$_2$ atmosphere.

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