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Selective coupling of carbon dioxide and epoxystyrene via salicylaldimine-, thiophenaldimine-, and quinolinaldimine-iron(II), iron(III), chromium(III), and cobalt(III)/Lewis base catalysts

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Abstract A series of chromium(III)-, cobalt(III)-, and iron(III)-based complexes of the general formula $[(N\cap O)_2MCl]$ (**1–7**) ($N\cap O$: *N*-salicylidene(R)amine, R = 1-naphthyl or cyclohexyl) have been applied as catalysts for the coupling reaction of carbon dioxide and epoxystyrene (styrene oxide) in the presence of tetrabutylammonium bromide (Bu_4NBr) as a cocatalyst. The reactions were carried out under relatively low pressure and solvent-free conditions. In addition, iron complexes (**8–10**) containing the ligands, *N*′-(thiophene-2-methylene)benzene-1,2-diamine, (**8**), *N*′-(quinoline-2-methylene)benzene-1,2-diamine (**9**), and sodium *N*-(4-sulfonato-salicylidene)-1,2-phenylenediamine (**10**) were also utilized for the catalytic reaction. The influence of metal center, ligand, temperature, and reaction time on the coupling reaction was investigated. The catalyst systems proved to be selective in the coupling reaction of CO_2 and styrene oxide, resulting in cyclic styrene carbonate. In general, the iron(III)- and cobalt(III)-based catalysts bearing the aromatic 1-naphthyl terminal groups showed the highest catalytic activity under similar reaction conditions.

Introduction

There is a growing effort to develop new chemical processes using biorenewable resources [1–3]. One such resource of particular interest is CO_2, a nontoxic, nonflammable, naturally abundant C_1 feedstock [4, 5]. The reaction of CO_2 with metal complexes has been extensively studied, revealing potential pathways for catalytic reactions [6–12]. However, the thermodynamic stability of CO_2 has hindered its utility as a reagent for chemical synthesis; in fact, its high stability makes it an ideal medium for many chemical processes [13, 14]. To overcome this limitation, reactions employing CO_2 with highly reactive reagents have been explored. In particular, the catalytic coupling of CO_2 with heterocycles has received considerable attention over the past years [15–17]. A majority of these publications involve the reaction of CO_2 with epoxides to generate polycarbonates and/or cyclic carbonates (1,3-dioxolan-2-ones) [18–22].

Aliphatic polycarbonates have potential applications as packaging materials, as well as in the synthesis of engineering thermoplastics and resins [23, 24]. Poly(propylene carbonate) decomposes uniformly and controllably to cyclic propylene carbonate below 250 °C [25, 26], making it particularly useful as a binder for ceramics, adhesives, and propellants [27]. Furthermore, cyclic carbonates are valuable as solvents [28] and are also important intermediates for the synthesis of fuel additives [29], pharmaceuticals and fine chemicals [30].

The most common catalyst precursors reported for the synthesis of both cyclic carbonates and polycarbonates are based on Co(III) [31, 32] and Cr(III) [33] complexes with tetradentate salen and porphyrin ligands. Square pyramidal geometry is characteristic of both salen and porphyrin complexes. This involves planar coordination of the ligand framework around the metal center with the square pyramid coordination sphere being completed by a halide at the apical position.

Numerous catalytic systems have been developed for the synthesis of cyclic carbonates; among these catalysts, salen

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complexes of chromium [33], cobalt [34], ruthenium [35], zinc [36–39], aluminum [40, 41], and tin [42] have showed high catalytic activity. However, some of these metals are highly toxic, especially the commonly used cobalt and chromium complexes, which limit the potential application of the resulting product species.

Lately, there have been reported on the application of unbridged, iodo bis(aldiminato) and bis(ketiminato) cobalt(III) complexes for the coupling of styrene oxide and CO_2 [43]. The bis(phenoxyiminato) Co(III) complex catalyzed with tetrabutylammonium bromide (Bu_4NBr) produced cyclic styrene carbonate, while with 4-dimethylaminopyridine (DMAP), oligomers were formed together with the cyclic product. Nevertheless, only limited studies about the utilization of iron-based catalysts for the coupling reaction of epoxide and carbon dioxide have been reported [44, 45]. Rieger and coworkers reported recently on the successful application of an octahedral iron(II) complex bearing a tetradentate nitrogen ligand for the conversion of propylene oxide and CO_2 to cyclic propylene carbonate [46].

Recently, we reported the synthesis of some transition metal-based complexes bearing different salicylaldimine, thiophenaldimine, and quinolinaldimine ligands containing aromatic and cyclic aliphatic terminals [47, 48]. The complexes have been utilized successfully as catalysts for polymerization of acrylate monomer [49]. High-molar mass poly(*tert*-butyl acrylate) polymers with very low molecular weight distributions (M_w/M_n up to 1.09) were isolated. In addition, it has been found that the polymerization reaction depends on the metal center, the auxiliary groups, and the substituents on the backbone of the ligand.

In the present study, we report on the utilization of the above iron(III) (**4**, **5**, **10**) and iron(II) (**8**, **9**) complexes for the coupling reaction of carbon dioxide and styrene oxide. For comparison reasons, the corresponding Cr(III) (**1–3**) and Co(III) (**6**, **7**) complexes have also been used. Using the bis(salicylaldimine) ligands, the iron(III) complexes showed the highest catalytic activity. In addition, the thiophenaldimine iron(II) complex (**8**) showed a notable performance for the catalytic reaction compared with the commonly used conventional trivalent Cr(III)-based complexes.

Experimental

All reactions were carried out under dry nitrogen using standard Schlenk techniques. Styrene epoxide and tetrabutylammonium bromide (Bu_4NBr) were purchased from Aldrich and used as received without any further purification. The complexes **1–10** were prepared by following previously published procedures [49, 50].

Elemental analyses were performed at the Hashemite University (EURO EA 3000 instrument). ^{1}H-NMR spectra were recorded on a Bruker spectrometer operating at 300 MHz using $CDCl_3$ as a solvent with TMS as an internal standard. ^{13}C-NMR spectra were obtained on a Bruker spectrometer operating at 75 MHz. Infrared spectra were measured on a Nicolet Magna-IR 560 spectrophotometer. GC–MS was measured on a Varian CP-3800 GC unit with a Varian Saturn 2100 T mass spectrometer (column: PDMS with 5 % phenyl (DB-5)). *In situ* IR measurements were performed with a Mettler-Toledo system with DiComp windows under argon.

Typical reaction procedure

The coupling reactions were conducted in a 300 or 100 ml stainless steel autoclave equipped with a glass vessel and a magnetic stirring bar. In a typical reaction setup, the catalyst, cocatalyst, and epoxide (1/1/2556) were loaded. The reactor was then pressurized with the appropriate amount of CO_2 and heated to the desired temperature. After the required reaction time, the reactor was cooled and the gases were vented off. The solvents were evaporated, and the residue was taken up in CH_2Cl_2. This solution was passed over a short silica gel column to remove catalyst residues. Evaporation of the solution gave the product as a white powder.

Cyclic styrene carbonate: EA: found (Calcd)(%): C, 65.92 (65.85); H, 4.61 (4.91). GC/MS: (164.8, 46 %); IR (cm^{-1}, KBr): av. ~1,776 (ν CO). ^{1}H NMR ($CDCl_3$): $\delta = 4.34$ (t, $J = 8.1$ Hz, 1H, CH_2), 4.80 (t, $J = 8.3$ Hz, 1H, CH_2), 5.68 (t, $J = 7.8$ Hz, 1H, CH), 7.37–7.43 (m, 5 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 71.1$ (CH_2), 77.9 (CH), 154.8 (CO) ppm (CO).

Results and discussion

Bis(salicylaldimine)-based chromium(III), iron(III), and cobalt(III) complexes (**1–7**) and thiophenaldimine-, quinolinaldimine-, and sodium salicylaldimine-iron(II) complexes [49, 50], (**8–10**) (Fig. 1) were activated by Bu_4NBr and utilized for the coupling reactions of styrene epoxide and carbon dioxide without added solvent at variable reaction temperatures and periods. The results are summarized in Table 1.

The influence of metal center, electronic properties of the ligand, temperature, pressure, and reaction time on the coupling reaction was investigated. The activities of the catalysts (TOF: mol-product/mol-catalyst. h) were recorded after the purification of the isolated material.

The complexes used in the present study showed relatively high catalytic activity and extreme selectivity toward the production of the target molecule (cyclic styrene carbonate) at quite low pressure (Table 1).

The cocatalyst alone showed also a moderate activity toward the coupling reaction (TON = 432). The obtained carbonates were analyzed by NMR, GC/MS, elemental analysis, and IR techniques. The IR spectra (neat) of cyclic styrene carbonate displayed a strong absorption band at around 1,776 cm^{-1}, which can be ascribed to the cyclic carbonate carbonyl group. No spectroscopic indication was found for the formation of poly(styrene carbonate) [50]. The ^{1}H NMR spectrum of the cyclic product exhibits resonances at 4.34 (1H, t) ppm, 4.80 (1H, t) ppm, 5.68 (1H, t) ppm, and 7.37–7.43 (5H, m) ppm, corresponding to the CH, CH_2, CH_2, and aromatic group, respectively. According to GC–MS, only one component which corresponds to cyclic styrene carbonate (molar mass = 164.8) was observed. The ^{13}C NMR spectra show signals at 71.1, 77.9, and 154.8 ppm, which can be attributed to the CH_2, CH, and CO, respectively.

Complexes **4** [$(Sal\text{-}Nap)_2FeCl$] and **6** [$(Sal\text{-}Nap)_2CoCl$], where the bis(salen) ligand carries the bulky aromatic naphthyl substituents, exhibit the highest turnover number under similar reaction conditions (TON = 1,767, 1,756, respectively).

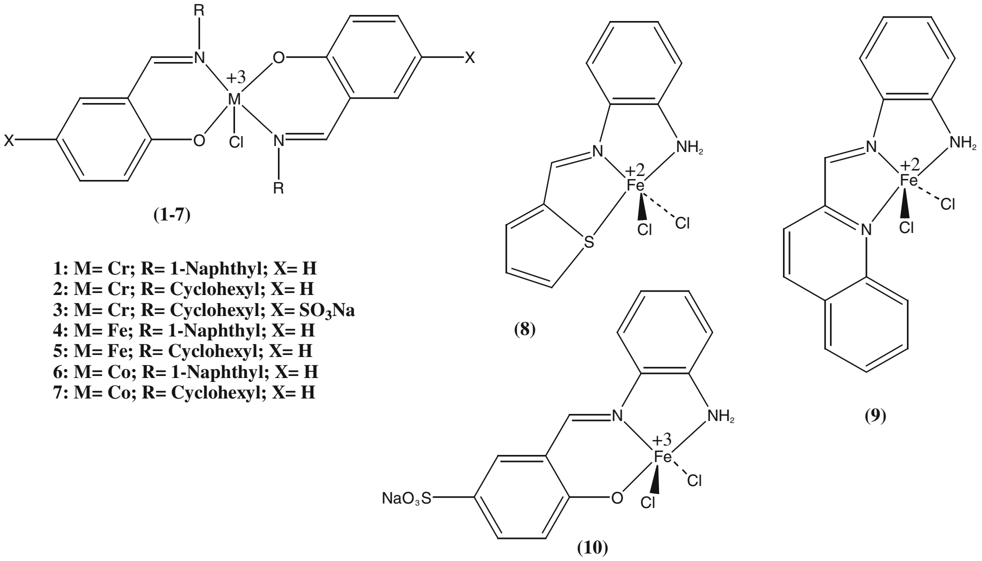
Iron(III)- and cobalt(III)-based catalysts with the bulky aromatic naphthyl groups showed the highest catalytic activity compared with the corresponding complexes bearing cyclohexyl terminal groups (**5** and **7**, respectively) or those of Cr(III)- and iron(II)-based complexes. This could be due to the increase in the steric effect around the metal center due to the presence of the bulky cyclohexyl terminal groups [51]. In general, differences in the ligand substitution pattern led to a slight effect on catalytic activity. The activity of the previously reported cobalt(III)-based catalyst system, bis{2-[(benzylimino)ethyl]phenoxy} iodo cobalt(III)/Bu_4NBr, is 640 mol cyclic styrene carbonate/mole catalyst [43]. The coupling reaction was carried out in dichloromethane at 145 °C and 10 bar of CO_2 for 1 h.

However, the metal center and its oxidation number showed a remarkable influence on the activity (Table 1). Under similar reaction conditions, iron(II) complexes showed lower activity toward the coupling reaction of styrene oxide compared with the more electrophilic iron(III)-based complexes (Fig. 2).

Utilizing the catalyst system [$(Sal\text{-}Nap)_2FeCl$], (**4**), the influence of the variables, temperature, reaction time, and pressure was investigated. The turnover number was increased by increasing both the reaction time and temperature (Table 1), while a dramatic decrease in the activity was observed at 1 atm pressure (Table 1, entry 5).

Experiments were performed at different temperatures in order to observe the reaction progress. It is well established that higher temperatures generally lead to enhanced production of cyclic carbonates [51]. Using the bis(salicylaldimine)-based catalyst system **4**, the formation of cyclic styrene carbonate was selective even at ambient temperatures (Table 1).

Because of the electron-withdrawing nature of the aromatic ring, it is possible that cyclic styrene carbonate is predominantly produced via backbiting of the propagating polycarbonate anion to the benzyl carbon of the adjacent carbonate unit [18, 51]. To gain an insight into the process of formation of cyclic styrene carbonate, the coupling reaction was carried out in situ in an FTIR autoclave using complex **4** under similar reaction conditions. The reaction progress was monitored every 30 s for the first 4 h (Fig. 3). The reaction can be followed by monitoring the absorption of the CO stretching vibration of cyclic styrene carbonate



1: M= Cr; R= 1-Naphthyl; X= H
2: M= Cr; R= Cyclohexyl; X= H
3: M= Cr; R= Cyclohexyl; X= SO_3Na
4: M= Fe; R= 1-Naphthyl; X= H
5: M= Fe; R= Cyclohexyl; X= H
6: M= Co; R= 1-Naphthyl; X= H
7: M= Co; R= Cyclohexyl; X= H

Fig. 1 Structures of the complexes used in the present study (**1**–**10**)

Table 1 Results of coupling reactions of styrene oxide with carbon dioxide using Cr(III)-, Fe(III)-, Co(III)-, and Fe(II)-based complexes

Entry	Complex	Complex no.	TON	TOF	Temperature (°C)
1	[(Sal-Nap)$_2$CrCl]	**1**	1,527	63.6	130
2	[(Sal-Cyc)$_2$CrCl]	**2**	840	34.9	130
3	[(Na-Sal-Nap)$_2$CrCl]	**3**	853	35.5	130
4	[(Sal-Nap)$_2$FeCl]	**4**	1,767	73.6	130
5	[(Sal-Nap)$_2$FeCl][a]	**4**	115	4.81	130
6	[(Sal-Nap)$_2$FeCl][b]	**4**	1,462	208.8	130
7	[(Sal-Nap)$_2$FeCl][b]	**4**	1,666	34.7	130
8	[(Sal-Nap)$_2$FeCl][b]	**4**	2,071	28.8	130
9	[(Sal-Nap)$_2$FeCl]	**4**	64	2.7	25
10	[(Sal-Nap)$_2$FeCl]	**4**	84	3.5	40
11	[(Sal-Nap)$_2$FeCl]	**4**	533	22.2	80
12	[(Sal-Cyc)$_2$FeCl]	**5**	1,506	62.7	130
13	[(Sal-Nap)$_2$CoCl]	**6**	1,756	73.2	130
14	[(Sal-Cyc)$_2$CoCl]	**7**	1,461	60.9	130
15	[(Thio-PDA)FeCl$_2$]	**8**	799	33.3	130
16	[(Quino-PDA)FeCl$_2$]	**9**	279	11.6	130
17	[(Na-Sal-PDA)FeCl$_2$]	**10**	107	4.5	130

Reaction conditions: ratio of cat./cocat (tetrabutylammonium bromide)/styrene epoxide = 1/1/2556; CO$_2$: 5 bars; TON: mole product/mole-cat.; TOF: mole product/mole cat. h

[a] 1 bar of CO$_2$

[b] Entries 6-8: reactions were carried out for 7, 48, and 72 h, respectively

and increases in intensity with increasing the amount of styrene carbonate formed over the course of the reaction. Based on the above data (Fig. 3), it seems that the formation of a (monomeric) cyclic styrene carbonate takes place via CO$_2$ insertion followed by the occurrence of a backbiting mechanism aided by the central metal ion [18, 51]. No polymer formation was observed during the whole reaction time.

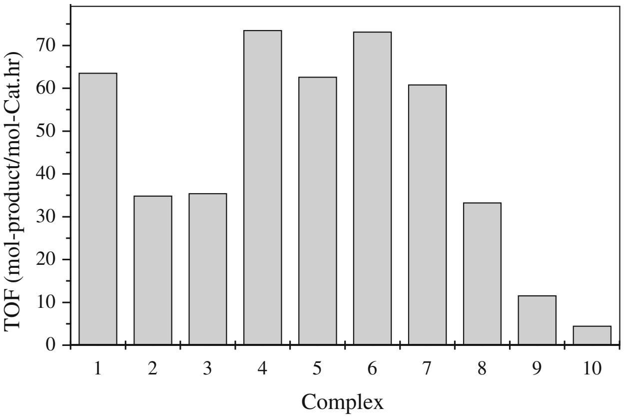


Fig. 2 Catalytic activity of Cr(III), Fe(III), Co(III), and Fe(II) complexes **1–10**

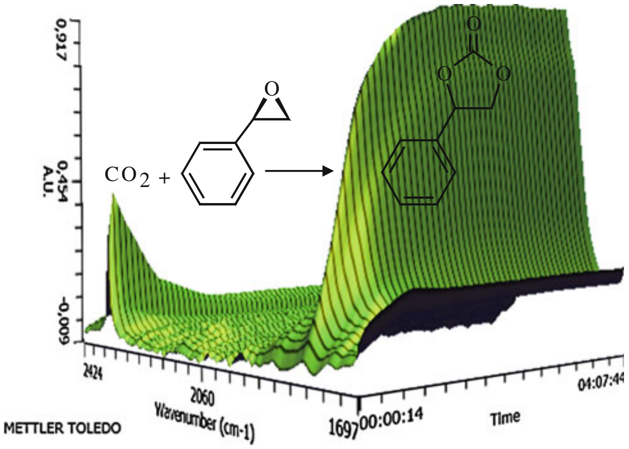


Fig. 3 FTIR spectra of the synthesis of styrene carbonate from styrene oxide in neat as a function of time using complex **4**

Cr(III) catalyst (**3**) that contains sodium sulfonato groups on the *para* position of the phenyl groups of the salen ligand showed lower activity compared with the corresponding sulfonato free, Cr(III) catalyst (**1**) (Table 1). This could be attributed to the lower solubility of complex **3** in the reaction media.

Iron(II) complex (**8**) with the thiophene donor ligand showed lower activity (TOF = 33.3, entry 15) than the bis(salicylaldimine)-based iron(III) and Co(III) complexes, but comparable with those of Cr(III)-based catalysts (**2** and **3**). In addition, it showed much higher catalytic activity than the corresponding quinolinaldimine (TOF = 11.6, entry 16)- and salicylaldimine (TOF = 4.5, entry 17)-based complexes.

Conclusion

In summary, a series of Cr(III), Fe(III), and Co(III) transition metal complexes bearing salicylaldimine-based ligands and iron(II) complexes with thiophenaldimine and quinolinaldimine ligands have been investigated as catalyst precursors for the coupling reactions of styrene oxide and carbon dioxide after activation with Bu$_4$NBr. The catalyst system was highly selective for the production of cyclic styrene carbonates. No polymer was formed during the process as supported by an in situ IR measurement, NMR spectroscopy, as well as GC–MS. The salicylidene-based iron(III) complexes are the most active toward the catalytic reaction. In addition, the complexes bearing the aromatic naphthyl terminal showed higher catalytic activity compared with those with the aliphatic cyclic terminals. Phenylenediamine-based iron(II) complexes showed lower activity, except the thiophenaldimine-based complex (**8**), which showed a comparable activity with Cr(III)-based catalysts presented in this study. Such costefficient iron-based catalysts could be a greener alternative to the toxic metal complexes used until now.

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