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A One-Component Iron Catalyst for Cyclic Propylene Carbonate Synthesis

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The development of a new tetraamine–iron complex as a catalyst for the cyclization of propylene oxide with carbon dioxide to form propylene carbonate is reported. The structure of the complex was confirmed by X-ray crystallography. The molecule exhibited an exceptionally long iron–chlorine bond and a high catalytic activity even without the addition of an activator. However, kinetic studies showed a second-order dependence on catalyst concentration. By using iron, we provide an ecologically as well as economically favourable alternative to the preferentially used toxic metals cobalt and chromium. On the basis of the kinetics and other experimental data, the catalytic cycle deduced as well as an understanding of the high activities.

Introduction

Climate change is generally linked with an increase in the amount of CO_2 in the atmosphere, which has dramatically risen due to the generation of energy by the combustion of fossil fuels.[1–3] Thus, one of the major challenges of the coming decades is to reduce the level of atmospheric carbon dioxide and therefore to decelerate or anticipate the effects of climate change.[4,5] Therefore the global chemical community faces two main challenges: to develop new methods to create sustainable raw materials from regenerative sources to decrease the impact of crude oil[4,6–8] and to make new energy sources and carriers accessible.[9–11] An urgent solution to these problems is required as current predictions suggest that the world-wide emission of CO_2 from fossil fuels such as gas or oil will peak in 2020.[12] Therefore CO_2 is an abundant, easily accessible and cheap raw material. Thus, CO_2 emissions can be used as a "regenerative" C_1 feedstock that can replace oil-based raw materials.[13] However, this approach will have no perceptible effect upon the level of atmospheric CO_2. To date, two compounds synthesized from CO_2 have industrial importance: salicylic acid has been prepared for over a century[14,15] and urea is prepared from CO_2 on a 100 million ton scale per annum.[16–18] Another commercially important process is the production of polymeric and cyclic carbonates.[8,19–21] Cyclic carbonates can be used as intermediates for polycarbonates,[22,23] electrolytes in lithium ion batteries or as green solvents.[24,25] Cyclic ethylene and propylene carbonates have been synthesized commercially from oxiranes and carbon dioxide since the 1950s.[19–21] Numerous catalytic systems have been developed for the synthesis of cyclic carbonates; onium compounds,[21,26,27] metal halides[28] and supported metal halides on zeolites, carbon and alumina,[29–33] lanthanide oxychlorides and transition-metal complexes. Among these catalysts, salen complexes of aluminium,[34–37] chromium,[37–39] cobalt,[39–42] zinc[43–46] and tin[47] and porphyrin and phthalocyanine complexes of aluminium[30,48] show high catalytic activities. However, some of these metals are highly toxic, especially the commonly used cobalt and chromium complexes, which limits the potential application of the resulting product species. In most cases an excess of co-catalyst (typically amines such as DMAP or onium salts such as tetrabutylammonium bromide) is essential for the activity of the catalysts.[34] The co-catalyst plays a key role in the catalytic cycle as the anion acts as a nucleophile and ring-opens the oxirane or labilizes the *trans*-coordinated ligands.[46] Reports of one-component metal–organic catalysts for cyclic carbonate synthesis are rare in the literature.[45,49–51] As an example, an active bimetallic aluminium salophen catalyst for cyclic carbonate synthesis has been created by North and co-workers by incorporating four tetraalkylammonium bromide units into the outer sphere of the complex.[45]

Herein we report the synthesis and catalytic activity of a single-component catalyst with a new ligand motif based on iron.

Results and Discussion

The procedures for the preparation of ligands and complexes are shown in Scheme 1.

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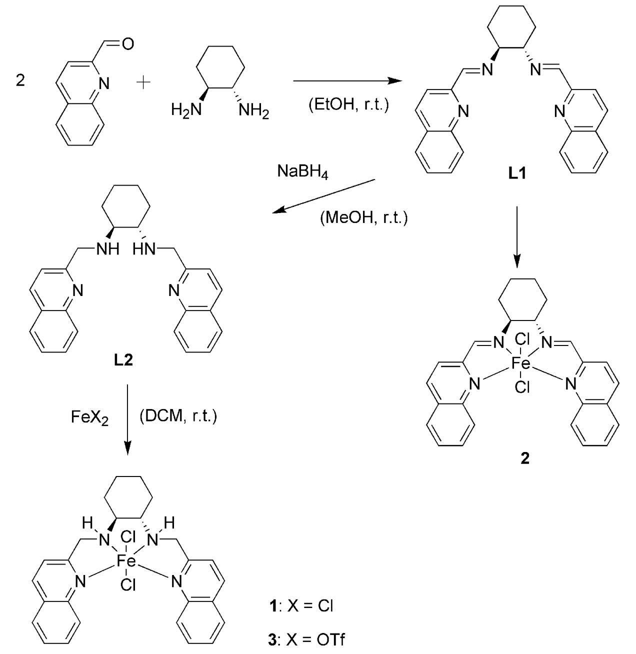


Scheme 1. Synthesis of catalysts **1** and **2**.

Ligand L1 is a Schiff base produced by the condensation of (*S*,*S*)-1,2-diaminocyclohexane with quinaldine-2-aldehyde at room temperature in ethanol. The hydrogenation of L1 to form L2 was performed with $NaBH_4$ in methanol.[52–54] The ligands were characterized by high-resolution mass spectrometry and ^1H and ^{13}C NMR spectroscopy. Complex **2** was synthesized according to a literature procedure.[55] By stirring ligand L2 in DCM with $FeCl_2$, **1** was obtained in quantitative yield as red crystals. IR spectroscopic analysis of the resulting complex showed a broadening of the N–H stretching vibrations after complexation (see the Supporting Information). In the FIR region, strong bands at 232, 269 and 320 cm^{-1} are observed, which can be assigned to iron–nitrogen vibrations. Fe–Cl stretching modes are observed at 195 cm^{-1} (Figure 1).[56,57]

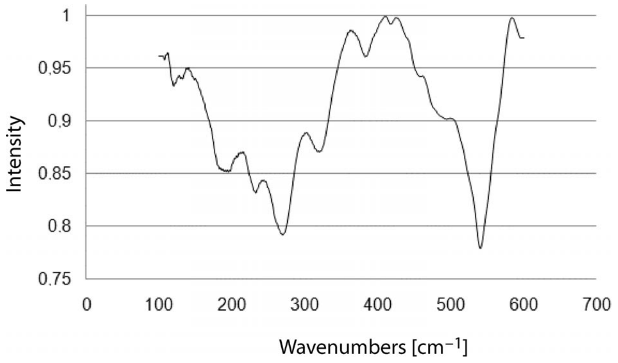


Figure 1. FIR spectra (Nujol suspension) of compound **1** in the range of 100–600 cm^{-1}.

A priori, the tetradentate ligands of this architecture can adopt three different topologies with the chloride in *trans*, *cis*-α and *cis*-β positions (Figure 2). NMR spectroscopic and X-ray diffraction studies show that complex **1** forms a *trans* topology in the crystal as well as in solution.

Figure 2. Three possible topologies for compound **1**.

For tetradentate ligands in which the two internal donors are secondary or tertiary amines, *cis*-β or mixtures of *cis*-α and *cis*-β isomers are typically obtained. Related Fe^{II} and Fe^{III} complexes with tetradentate ligands with pyridyl or quinoline donors mostly adopt a *cis*-α structure in both mono- and bimetallic complexes because these conformations are energetically preferred.[58–61] Only a few *trans* structures, usually with very rigid backbones that force a *trans* geometry, have been detailed in the literature up to now.[62–70] A single crystal suitable for X-ray diffraction analysis was obtained by slow diffusion of pentane into a chloroform solution of complex **1**. The ORTEP diagram of the structure is shown in Figure 3. Unlike the *cis* topologies of the Fe^{II} complexes obtained with tertiary amines or mixed ligands with secondary and tertiary amines, the molecule shows a planar or *trans* topology, which is usually known for ligands with very rigid backbones or Schiff base ligands.[71] A single-crystal X-ray structure analysis of **1** proves the desired chiral and C_2-symmetric complexation of the tetradentate ligand L2. The Fe–Cl bond lengths are 2.495(1) and 2.509(1) Å, longer than is expected for Fe^{II}–

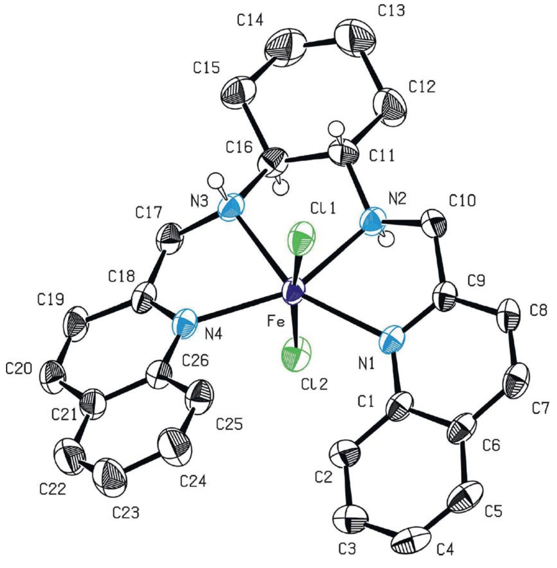


Figure 3. ORTEP style plot of compound **1** in the solid state. Hydrogen atoms have been omitted for clarity except those bound to the chiral centres N2, C11, C16 and N3. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Fe–Cl1 2.495(1), Fe–Cl2 2.509(1), Fe–N1 2.187(2), Fe–N2 2.197(3), Fe–N3 2.193(3), Fe–N4 2.213(3); Cl1–Fe–Cl2 172.90(3), Cl1–Fe–N1 84.87(7), Cl1–Fe–N3 95.50(8), N1–Fe–N2 74.8(1), N2–Fe–N3 78.0(1), N3–Fe–N4 74.5(1), Cl2–Fe–N2 87.76(8).

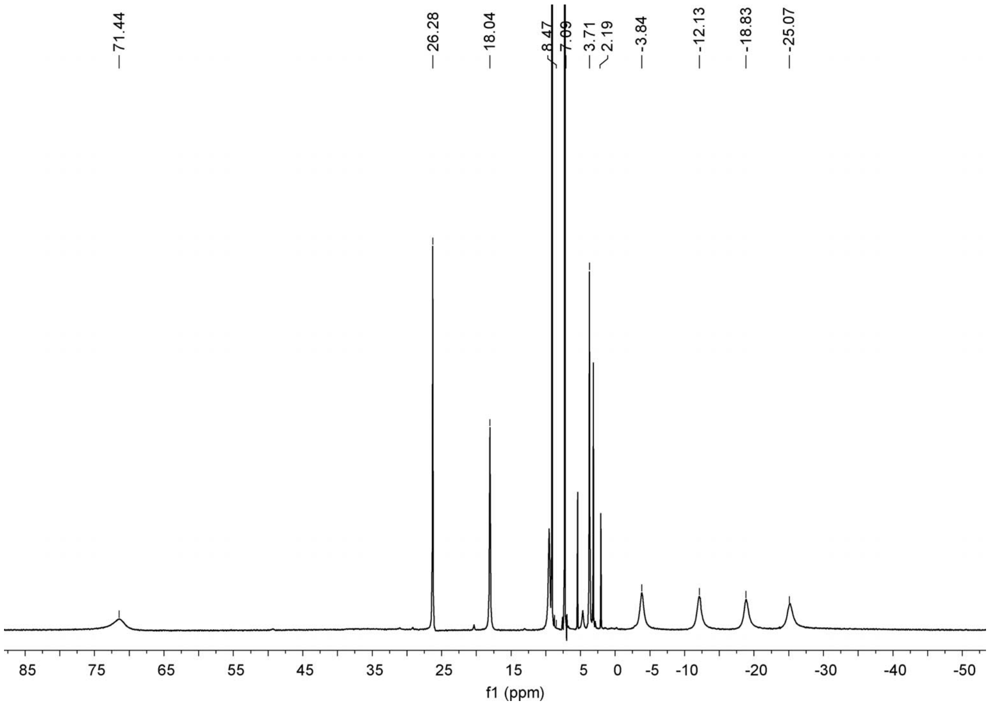


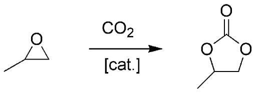
Figure 4. ^1H NMR of compound **1** at room temperature in $[D_2]$DCM in the range of –30 to 80 ppm.

tetraamine complexes [e.g., 2.397(2)[72] and 2.401(2) Å[60]] and therefore the Fe–N bonds, at 2.187(2), 2.197(3), 2.193(3) and 2.213(3) Å, are shorter than expected for the corresponding complexes of tertiary amines.[60,73,74] The coordination geometry around the Fe^{II} centre is not ideally octahedral due to the high degree of ring strain imposed by the three adjacent five-membered metallacycles and the chemically differing nature of the nitrogen atoms. On steric grounds, the planes of the quinaldine units (C18–C26, N4 and C1–C9, N1) enclose an angle of 17° with each other and provide a chiral cage around the iron centre. The Cl1–Fe–Cl2 bond angle of 172.90(3)° shows a near-axial orientation; the deviation from the ideal value of 180° is proposed to be a result of crystal packing effects.

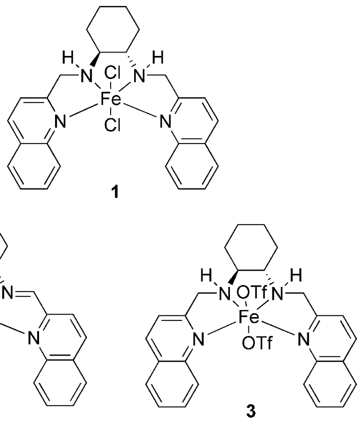
The ^1H NMR spectra of compound **1** shows that the iron(II) chloride *trans*-*N*,*N′*-bis(quinolin-2-ylmethyl)cyclohexane-1,2-diamine exists as a single isomer. Figure 4 clearly shows only one set of signals corresponding to the 11 protons of complex **1**. The NMR spectra suggest that both **1** and **2** retain their respective ligand topologies in solution. Even heating at 50 °C for 12 h in DCM showed no interconversion between any proposed structures.

Cyclization of Propylene Oxide with Carbon Dioxide

The standard test reaction was the conversion of propylene oxide to cyclic propylene carbonate (Scheme 2) and complexes **1**–**3** (Scheme 3) were applied as catalysts in this reaction.



Scheme 2. Cyclization of propylene with CO_2.



Scheme 3. Structural formulae of complexes **1**–**3**.

All reactions (except kinetic measurements) were performed without the addition of solvent in 100 mL autoclaves. The reactions were performed with compounds **1**–**3** at 100 °C and 15 bar CO_2 pressure; the results are summarized in Table 1. Under the applied conditions, no reaction was observed without the use of a catalyst (entry 1). Complexes **1** and **3** exhibited high activities at elevated temperatures without the addition of a co-catalyst (entries 2 and 4). A striking feature of these experiments was the inactivity of the diimine complex **2**. The asymmetric units of the ligand backbone had no visible effect on the enantiofacial discrimination of the carbonate formed, as was proven by chiral GC. The reactions were selective yielding cyclic carbonates with propylene oxide, as shown by GC–MS.

Table 1. Catalytic cyclization of propylene oxide and CO_2 with compounds **1**–**3**.[a]

Entry	Compound	Conversion [%]
1	TBAB	traces
2	**1**	80
3	**2**	traces
4	**3**	41
5	**1** + TBAB	100
6	**2** + TBAB	82
7[b]	**1** + TBAB	82
8	**1** + DMAP	58
9	**1** + PPNCl	77
10	**1** + MeIm	43

[a] Conditions: 1 mol-% catalyst, 1 mol-% co-catalyst when employed, 100 °C, 15 bar CO_2, 2 h. [b] Conditions: 1 mol-% catalyst, 1 mol-% co-catalyst, 100 °C, 15 bar CO_2, 1 h. Conversions were determined by ^1H NMR spectroscopy.

With co-catalyst tetrabutylammonium bromide (TBAB), which has been demonstrated to be effective in accelerating cyclization reactions in combination with metal–organic compounds, **2** demonstrated increased reactivity with conversions of up to 82% within 2 hours. Use of other co-catalysts like DMAP, PPNCl and methylimidazole resulted in a decrease in reactivity. The reaction speed decreased in correlation with the nucleophilicity of the resulting amines. It is supposed that the in situ nucleophilic amines coordinate to the iron centre and decelerate the reaction speed.

The conversions of the cyclization reaction under different reaction conditions are presented in Table 2. These results are in accord with the kinetic measurements presented in the next section.

Table 2. Catalytic cyclization of propylene oxide and CO_2 with compound **1** under different reaction conditions.

Entry	Temp. [°C]	CO_2 pressure [bar]	Catalyst conc. [mol-%]	Conv. [%][a]
1	100	15	1.0	80
2	100	15	1.5	100
3	100	15	0.5	31
4	100	30	1	100
5	80	15	1	57
6	60	15	1	26

[a] Determined after 2 h by ^1H NMR spectroscopy.

Kinetic Measurements

To gain an insight into why the iron catalysts demonstrate such high activity, a kinetic study of the formation of cyclic propylene carbonate catalysed by complex **1** was undertaken. The analysis was performed in situ in an FTIR autoclave. As the catalyst exhibits limited solubility in propylene oxide, a solvent had to be used for these reactions to ensure homogeneity of the reaction medium. DCM was identified as the ideal candidate. The reaction progress was monitored every minute for 8 h. Figure 5 shows a typical plot for the reaction under standard reaction conditions. The reaction can be followed by monitoring the absorption at 1791 cm^{-1}, which corresponds to the C=O stretching mode of cyclic propylene carbonate and increases in intensity with increasing amounts of propylene carbonate formed over the course of the reaction. North and coworkers[75] showed that the reaction under solvent-free conditions is pseudo-zero order whereas in solvent it is first order with respect to the starting material. In agreement with these observations, the reaction kinetics in DCM were determined to be first order with respect to the starting material, as shown in Figure 5.

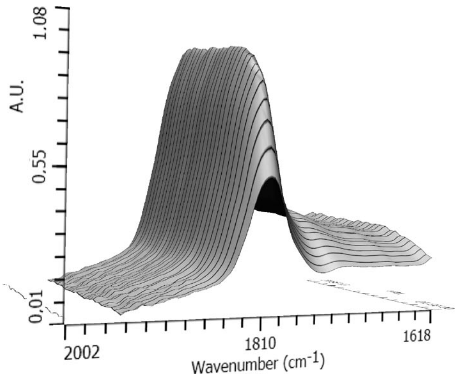


Figure 5. FTIR spectra of the synthesis of propylene oxide from propylene carbonate in DCM as a function of time (1.1 mL 1 mol-% propylene oxide, 3 mL DCM, 15 bar CO_2 at 100 °C).

An important aspect of the chromium-catalysed asymmetric ring-opening reaction is that the complex serves as a catalyst that activates both the nucleophile and the electrophile in a bimetallic rate-determining step.[76–78] Thus, there is a second-order dependence on the catalyst concentration in the rate law of the asymmetric ring-opening reaction. In the copolymerization with Cr(salen), a similar second-order dependence was found.[79,80] To examine this dependence in the cyclization reaction catalysed by **1**, we carried out a kinetic study of this reaction as a function of catalyst loading. As noted in the report of Darensbourg et al., there is a short induction period to activate the catalyst.[80] Thus, to determine the initial rates, the slope of the linear section after the inflection point of the reaction profile was determined. To determine the order of the reaction with respect to the catalyst, the reaction was performed at constant temperature, CO_2 pressure and propylene oxide concentration at three different concentrations of complex **1**. Figure 6 shows the FTIR data recorded at concentrations of 0.5, 1.0 and 1.5 mol-% of the catalyst. The logarithmic plot of the initial rates of the cyclization reaction against catalyst concentration showed a linear dependence with a slope of two, which indicates a bimetallic reaction mechanism (Figure 7).

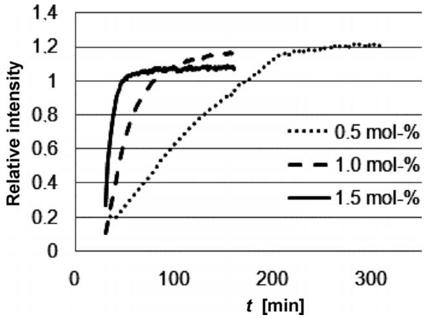


Figure 6. Comparison of the kinetics of the cyclic carbonate synthesis catalysed by complex **1** at different concentrations of catalyst (0.5, 1.0 and 1.5 mol-%).

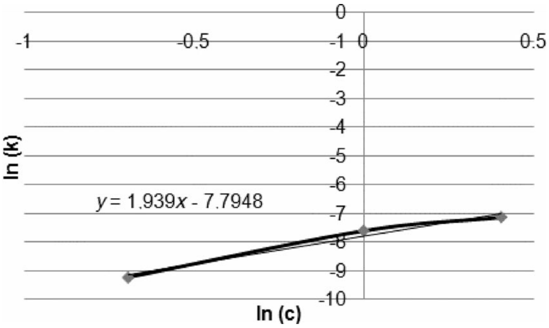


Figure 7. Logarithmic plot of the of the initial rates of the reaction against the catalyst concentration of complex **1**.

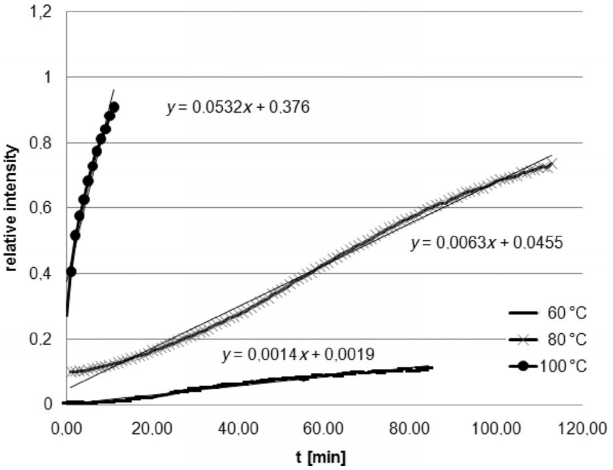


Figure 8. Comparison of the initial rates of the cyclic carbonate synthesis catalysed by complex **1** at different temperatures (60, 80 and 100 °C).

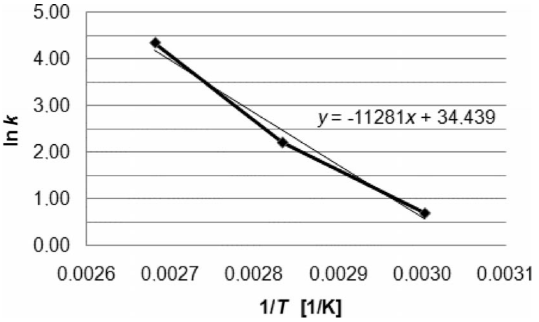


Figure 9. Arrhenius plot of the cyclic carbonate synthesis catalysed by complex **1**.

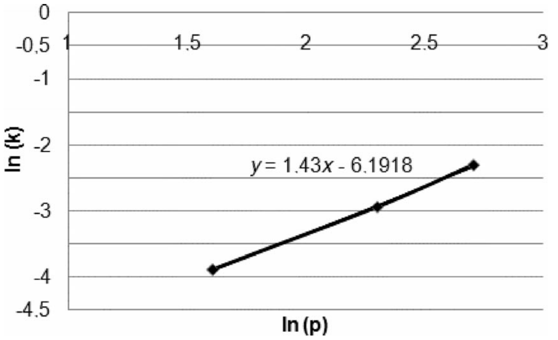
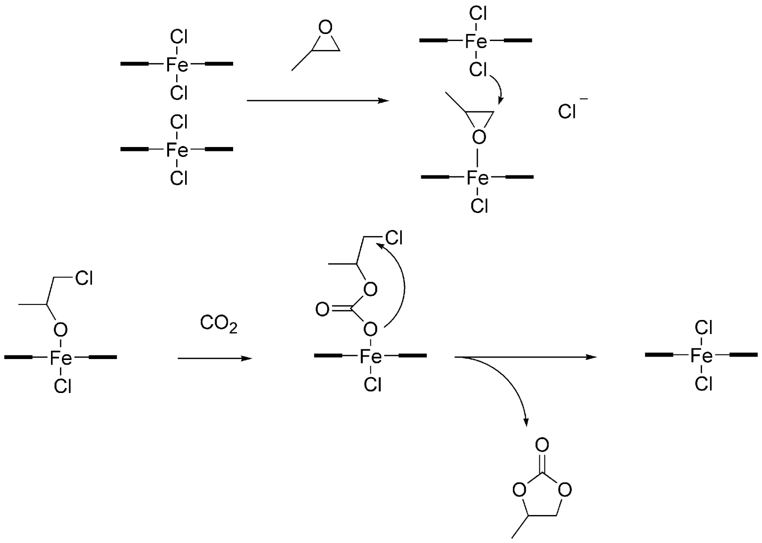


Figure 10. Plot of $\ln k_{obs'}$ against $\ln p(CO_2)$.

A clear influence of temperature on the reaction velocity was observed; the reaction rate increased with temperature, as shown in Figure 8. At 60 °C, a low reactivity was observed and a maximum reaction rate was found at 100 °C. The activation barrier for the formation of the cyclic carbonate can be derived from this kinetic data by an Arrhenius plot (Figure 9). By using this data, an activation barrier of $\Delta E_a = 93.8\ \mathrm{kJ\,mol^{-1}}$ was obtained. This result is in good agreement with the values obtained by Darensbourg et al. for the Cr(salen)-catalysed cyclization of propylene oxide with CO_2, which has a ΔE_a of $100.5\ \mathrm{kJ\,mol^{-1}}$.[80]

The order of cyclic carbonate formation with respect to carbon dioxide pressure can be determined by applying different pressures of CO_2 at constant temperature and catalyst concentration. As the rate of carbon dioxide dissolution in DCM is far higher than cyclic carbonate formation, a rapid equilibrium forming a constant CO_2 concentration in the solvent is established. The CO_2 concentration demonstrates (at low pressures) a linear dependence on the applied CO_2 pressure (5, 15 and 30 bar). The plot of $k_{obs'}$ against CO_2 pressure shows a linear dependence nearly passing through the origin, which indicates a single liquid phase and a linear dependence of the dissolved CO_2 on the pressure. The plot of $\ln k_{obs'}$ against $\ln p(CO_2)$ has a slope of 1.45 (Figure 10).

The question arises as to why catalysts **1** and **3** show such a difference in their activity in cyclic carbonate formation. Compound **1** demonstrates high activity whereas compound **2** is inactive towards the cyclization of CO_2 and propylene oxide. In combination with tetrabutylammonium bromide, compound **2** shows moderate activity. As demonstrated by North et al., the co-catalyst has two key roles in the catalytic cycle: to provide bromide for the nucleophilic ring-opening of the epoxide and to generate in situ tributylamine (TBA) for better CO_2 activation and coordination. TBA reacts with carbon dioxide to form a carbamate salt that delivers the gas.[46] The amine functionality should then be able to react with CO_2 to form a carbamate salt. To check whether this is the reason for the high activity, triethylamine was used as a co-catalyst with compound **2**,



Scheme 4. Mechanistic proposal for the cyclization reaction of carbon dioxide with propylene oxide.

but no reaction was observed. Therefore the activity of compound **1** must result from the possibility of a dissociation of a chloride ligand from the iron centre thereby forming a cationic iron species, which can coordinate PO, and a free chloride anion, which is then able to ring-open the epoxide. This theory is supported by the crystal structure of **1** which exhibits an extremely long and therefore labile iron–chlorine bond. This is also supported by a binuclear mechanism of the cyclization reaction. This was also concluded by Jacobsen and co-workers for the mechanism of the (salen)Cr-catalysed asymmetric ring-opening reaction in which the complexed chromium serves as a Lewis acid for epoxide binding/activation and simultaneously as the delivery agent for the nucleophile, which opens the epoxide.[76–78] On the basis of this information we propose a mechanistic model similar to those models proposed previously by Darensbourg and Yarbrough.[79] The weak Fe–Cl bond of **1** allows an attack of the epoxide on the iron centre and a second catalyst molecule opens the ring. After CO_2 insertion, back-biting process occurs which reforms the catalyst thus producing cyclic carbonate (Scheme 4).

Conclusions

We have presented a number of iron(II) complexes as new catalytic systems comprising an easily modified ligand motif with iron as the metal centre. The systems are active in cyclic carbonate synthesis through the coupling of CO_2 with propylene oxide. These compounds combine a number of important features: i. the iron–amine systems are reactive and have good stability that allows usage under elevated temperatures and therefore, due to the exothermic reaction, a reusage of the evolved reaction heat in industrial applications (e.g., for further distillation), ii. simple and easily accessible catalytic structures, iii. elimination of the need for a co-catalyst, which makes the reaction economically and ecologically favourable, and iv. due to the use of cost-efficient iron a greener alternative to the toxic metal complexes used until now. This combination of characteristics makes these catalyst systems attractive candidates for further academic and industrial research, especially in the copolymerization of CO_2 and epoxides to form polycarbonates.

Experimental Section

General: All reactions of air- and/or moisture-sensitive compounds and product manipulations were performed under dry argon using standard Schlenk techniques or in an inert atmosphere in a glovebox. All chemicals were purchased from Aldrich, Acros or ABCR. Solvents were obtained from a MBraun MB-SPS solvent purification system. Solution NMR spectra were collected at room temperature using a Bruker ARX300 spectrometer. ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent peak of $SiMe_4$. ESI-MS mass spectra were recorded with a Finnigan MAT 8200 spectrometer at 70 eV. FAB-MS were recorded with a double-focussed Finnigan MAT90 spectrometer. Infrared spectra were recorded with a Bruker IFS55 FT-IR spectrometer at room temperature. In situ IR measurements were performed with a Mettler–Toledo system with DiComp windows under argon. GC–MS was performed with a Saturn 2100 T GC–MS system with a Varian Factorfour capillary column (VF-5ms 30 m × 0.25 mm).

N**,*****N*****-Bis(quinolin-2-ylmethylene)-1,2-cyclohexanediamine (L1):** Quinaldine-2-aldehyde (3.09 g, 19.70 mmol) was diluted in ethanol (20 mL) and (*S*,*S*)-1,2-diaminocyclohexane (1.09 g, 9.6 mmol) was added. After a short time a yellow powder separated that was removed by filtration after 2 h. White crystals of L1 (3.3 g, 8.54 mmol, 89 %) were obtained after recrystallization from diethyl ether/DCM. ^{1}H NMR ($CDCl_3$, room temp.): δ = 1.57–1.90 (m, 10 H, cyclohexane), 3.56 (br., 2 H, methylene), 7.44–8.40 (m, 12 H, quinoline) ppm. ^{13}C NMR ($CDCl_3$, room temp.): δ = 24.58, 32.93, 74.06, 118.76, 127.33, 127.82, 128.91, 19.67, 136.55, 147.90, 155.16, 162.07 ppm. MS (EI): *m*/*z* = 392 $[M]^+$, 128 $[M - C_{17}H_{17}N_3]^+$.

N**,*****N*****-Bis(quinolin-2-ylmethylene)-1,2-cyclohexanediamine (L2): L1** (6.94 g, 17.68 mmol) was suspended in MeOH (60 mL) and cooled to 0 °C. Sodium borohydride (6.68 g, 176 mmol) was added slowly and the mixture stirred at room temperature for 12 h. The orange solution formed was filtered and the solvent removed in vacuo. Water (50 mL) was added and the product extracted with DCM. The organic phase was filtered through Na_2SO_4 and the solvent was removed under vacuum to yield a white solid (5.1 g, 73%, 12.9 mmol). The compound was spectroscopically clean and used without further purification. ^{1}H NMR ($CDCl_3$, room temp.): δ = 0.90–2.36 (m, 8 H, cyclohexane), 2.57 (br., 2 H, NH-C*H*), 3.95–4.20 (dd, 4 H, methylene), 7.39–8.00 (m, 12 H, quinoline) ppm. ^{13}C NMR ($CDCl_3$, room temp.): δ = 23.9, 30.6, 52.1, 60.5, 119.6, 124.8, 126.1, 127.8, 128.1, 135.1, 146.5, 160.1 ppm. MS (EI): *m*/*z* = 396 $[M]^+$, 254 $[M - C_{10}H_8N]^+$, 143 $[C_{10}H_9N]^+$.

[*N*,*N*-Bis(quinolin-2-ylmethylene)-1,2-cyclohexanediamine]iron(II) Chloride (1): An excess of $FeCl_2$ was added to a solution of *N*,*N'*-bis(quinolin-2-ylmethylene)-1,2-cyclohexanediamine (1 g, 2.5 mmol) in DCM. After stirring the suspension for 24 h, the deep-red solution was removed by filtration and the complex was precipitated by the addition of diethyl ether. The desired product was isolated as a deep-red powder in quantitative yield (1.29 g). Single crystals were obtained by diffusion of pentane in a solution of **1** in chloroform. ^{1}H NMR (CD_2Cl_2, room temp.): δ = 71.44, 26.28, 18.01, 8.07, 7.07, 3.71, 2.19, –3.81, –12.13, –18.83, –25.07 ppm. IR: $\tilde{\nu}$ = 3273 (N–H), 2923 ($C–H_{aromatic}$), 2857 ($C–H_{aliphatic}$), 301 (Fe–Cl), 224, 199 (Fe–N) cm^{-1}. MS (FAB): *m*/*z* = 486.6 $[M - Cl]^-$, 450.7 [M – 2 HCl]. $C_{26}H_{28}Cl_2FeN_4$ (532.28): calcd. C 59.68, H 5.39, N 10.71; found C 60.01, H 5.43, N 10.53.

[*N*,*N*-Bis(quinolin-2-ylmethylene)-1,2-cyclohexanediimine]iron(II) Chloride (2): Complex **2** was prepared and characterized according to the literature procedure.[81] Additional analysis: ^{1}H NMR (CD_2Cl_2, room temp.): δ = 55.2, 45.8, 17.4, 5.6, 1.9, 1.1, 0.8, –17.0, –17.5, –23.0, –26.3 (br) ppm.

[*N*,*N*-Bis(quinolin-2-ylmethylene)-1,2-cyclohexanediamine]iron(II) Triflate (3): An excess of $Fe(OTf)_2$ was added to a solution of *N*,*N'*-bis(quinolin-2-ylmethylene)-1,2-cyclohexanediamine (1 g, 2.5 mmol) in DCM. After stirring the suspension for 24 h, the yellow solution was removed by filtration and the complex was precipitated with diethyl ether. The desired product was isolated as a canary yellow powder in 53% (960 mg, 1.3 mmol) yield. ^{1}H NMR (CD_2Cl_2, room temp.): δ = 62.9, 21.2, 10.7, 6.5–9.5 (m), 1.85, –4.6, –12.4, –18.3, –27.9 ppm. MS (FAB): *m*/*z* = 601.2 [M – OTf], 450.2 [M –2HOTf]. $C_{28}H_{28}F_6FeN_4O_6S_2$ (750.51): calcd. C 44.81, H 3.76, N 7.47, S 8.54; found C 43.81, H 3.79, N 7.20, S 8.97.

General Procedure for the Catalytic Cyclization of Propylene Oxide and Carbon Dioxide to Give Cyclic Propylene Carbonate (Non-IR Measurements): The iron complex and propylene oxide were added to a 100 mL stainless-steel autoclave that had been heated to 130 °C in an oven and allowed to cool to room temperature under argon. CO_2 was added to this mixture to the desired pressure and the autoclave allowed to stabilize for several minutes. The reactor was then heated to the desired temperature and the reaction stirred for 2 h. Benzene (0.1 mL) was then added and the sample analysed by ^{1}H NMR spectroscopy in deuteriated chloroform and the yield was determined by using the added benzene as an internal standard.

General Procedure for Catalytic Cyclization of Propylene Oxide and Carbon Dioxide to Give Cyclic Propylene Carbonate (in situ IR Measurements): The catalyst and DCM were mixed in a Schlenk tube under a gentle flow of argon. Propylene oxide was added by syringe through a rubber septum. This mixture was added to the autoclave under argon. The reactors were heated to the desired temperature and the IR measurements were started. The autoclave was pressurized to the desired CO_2 pressure and IR measurements were taken every minute (each measurement consisting of 64 scans). The desired CO_2 pressure was regulated over the entire reaction time of 8 h. The amount of product formed was determined by integration of the area of the increasing C=O stretching bond.

Single-Crystal X-ray Structure Determination of 1: $C_{26}H_{28}Cl_2FeN_4{\cdot}3CHCl_3$, M_r = 881.38, crystal colour and shape: red fragment, crystal dimensions: 0.10 × 0.41 × 0.76 mm, crystal system: orthorhombic, space group: $P2_12_12_1$ (no. 19), *a* = 13.2698(4), *b* = 15.2660(5), *c* = 18.8254(8) Å, *V* = 3813.6(2) Å^3, *Z* = 4, μ (Mo-K_α) = 1.194 mm^{-1}, $\rho_{calcd.}$ = 1.535 $g\,cm^{-3}$, Θ range = 3.76–25.33, data collected: 50153, independent data [$I_0 > 2\sigma(I_0)$/all data/R_{int}]: 5712/6943/0.091, data/restraints/parameters: 6943/0/462, R_1 [$I_0 > 2\sigma(I_0)$/all data]: 0.0369/0.0474, wR_2 [$I_0 > 2\sigma(I_0)$/all data]: 0.0807/0.0832, GOF = 0.940, $\Delta\rho_{max/min}$: 0.49/–0.52 e Å^{-3}. For detailed information, see the Supporting Information.

CCDC-787632 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Details of the single-crystal X-ray structure determination of compound **1** and ^{1}H NMR spectra of compounds **2** and **3**.

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